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SYMPOSIUM ON LUBRICATION

A symposium on lubrication, organized by the local branches of The Chemical Society, The Institute of Petroleum, The Royal Institute of Chemistry, and The Society of Chemical Industry, was held in the Chemistry Lecture Theatre, The University, Manchester, on 19 April 1956. The chair at the morning session was taken by Professor G. Gee, F.R.S., the afternoon session was presided over by Professor F. Morton, a vice-president of The Institute of Petroleum, and the chairman at the evening session was Lt.-Col. S. J. M. Auld, O.B.E., M.C., President of The Institute of Petroleum.

THE FRICTION AND LUBRICATION OF SOLID SURFACES

By DR F. P. BOWDEN,* F.R.S. and DR J. W. MENTER *

SUMMARY

THE greater part of the frictional resistance between sliding surfaces is the force required to shear small junctions formed as a result of cold welding of a small number of surface asperities.

On this theory it should be possible to observe finite adhesions between metal surfaces placed in contact under normal loading. Earlier work by Dr McFarlane and Dr Tabor had shown that adhesion was indeed observed with the soft metal indium, and it was supposed that the absence of a measurable adhesion with harder metals was due to the presence of contaminant surface films (principally oxides) and the release of elastic stresses on removing the load, leading to a "peeling" effect on separation. Recent experiments by Dr Rowe have confirmed this view and have shown that when metal surfaces are denuded in a very high vacuum (10^{-5} μ) and the junctions are annealed after placing the metals in contact, strong adhesion can be observed with many harder metals (gold, nickel, platinum, silver). This adhesion can be increased further by tangential forces in accordance with the previous theory.

The strong adhesion between metals, increased by sliding, leads, even with surfaces not specially cleaned, to the transfer of metal from one surface to the other. The amount of this transfer has been measured by Dr Williamson using radioactive techniques. It is shown that in a number of common engineering operations transfer from the tool is appreciable and its significance is discussed.

The general picture of friction and metallic transfer described for metals has been found to be valid also for non-metallic materials. Among these the plastics are of particular practical importance. The plastic polytetrafluorethylene (PTFE) differs in an important respect from other materials in having a low friction even when no films are present on its surface. The use of PTFE as a low friction material is discussed.

It has been shown that during the sliding processes high temperatures may be developed locally at the sliding interface. The value of a number of temperature resistant non-metallic lubricants is discussed for use with surfaces which run hot or at high speed. Molybdenum disulphide is particularly effective when formed *in situ*. The frictional properties of graphite at high temperatures are discussed. *In vacuo*, a steady reduction in friction is observed as the temperature is raised, for graphite sliding on graphite, silver, and gold. With graphite on nickel, tungsten, or molybdenum, however, the fall in friction is arrested at about 1000° C, and a sharp increase is observed thereafter, which is attributed to the formation of metallic carbides at the surface.

In lubricated sliding when the relative sliding speeds are high the two surfaces are kept apart by a fluid film (hydrodynamic lubrication). An unusual example of quasi-hydrodynamic lubrication has been studied recently by Mr Freitay with dry metals sliding *in vacuo* at high relative speeds (~2000 m.p.h.). Extensive surface melting occurs, the molten metal acting as a liquid lubricant film giving a relatively low coefficient of friction.

With slow sliding speeds no hydrodynamic film is formed and surfaces must be separated by a solid boundary film in order to reduce friction and transfer. The boundary film must have a low shear strength and yet resist penetration in a direction normal to the surface. The behaviour of fatty acid and soap films as boundary lubricants is discussed, together with the effect of temperature on their ability to prevent metallic transfer between the sliding surfaces. The best boundary lubricants are those by which the surface is chemically attacked so that the film is formed *in situ* and is readily replenished when temporarily disturbed during sliding. The behaviour of

* University of Cambridge.

extreme pressure lubricants is essentially the same, *i.e.* a solid film of low shear strength, resistant to temperature rise, must be formed between the surfaces. Again, its efficiency is enhanced if the film is formed by chemical attack *in situ*.

Rolling friction is interesting in that it is unaffected by the presence of lubricants. Recent work by Dr Tabor has shown that this friction is attributable to hysteresis losses in cyclic deformation of the rolling surfaces. The role of the lubricant is to reduce intermetallic contact, and thus reduce wear of the contacting surfaces.

DISCUSSION

A. Cameron: The authors state that " with slow speeds no hydrodynamic film is formed."

We have been trying to find the limits of application of this type of lubrication, using an electric discharge method. It has been found that the potential difference with constant current discharging through a thin film is constant over about $\frac{1}{2}$ amp and is directly proportional to the film thickness. A static calibration rig gives about 0·2 volts, corresponding to 1×10^{-3} inches (Figs 1 and 2).

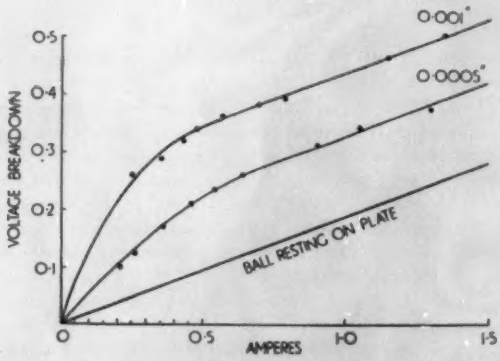

Fig 1

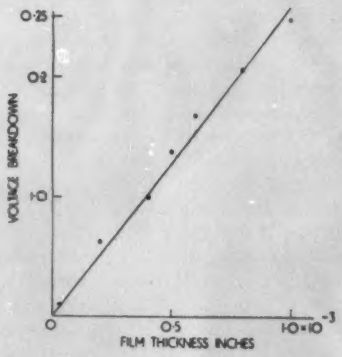

Fig 2

Using a four-ball machine with 1-inch balls, the friction and discharge potential were measured.

It was found that the coefficient of friction and the oil film thickness decreased with increasing load (Fig 3).

Experiments are now being carried out determining the limits of this hydrodynamic lubrication.

Have the authors encountered this oil film formation at these slow speeds and high loads?

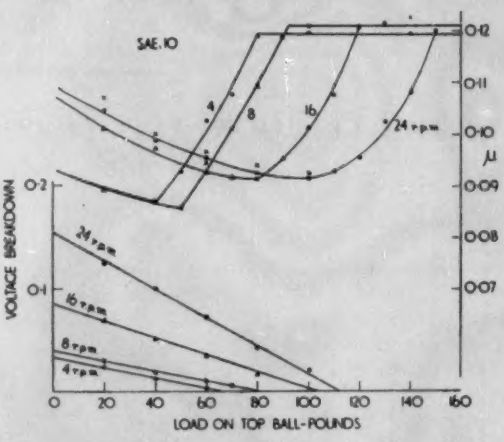

Fig 3

F. P. Bowden and J. W. Menter: In our work on the properties of boundary lubricants we have not observed any effects attributable to the formation of a fluid film. If the motion is intermittent, however, as occurs with a non-boundary lubricant, such as decane on steel, a slight reduction in μ is observed as the speed is increased in the range $10^{-2} \rightarrow 1$ cm/sec, due to the difference in the " stick " and " slip " friction.* From the values of μ shown by Dr Cameron, it would seem more appropriate to describe the lubrication as quasi-hydrodynamic, in which the conditions for film formation will be highly dependent upon such parameters as the pressure coefficient of viscosity of the lubricant and the surface finish of the contacting surfaces.

J. H. Harris: If a reactive metal surface, *e.g.* copper, has an oxide film only and is treated with a fatty acid, say, oleic in complete absence of water, if this is possible, would there be any reaction-forming soap?

F. P. Bowden and J. W. Menter: Dr. Tingle † showed that to obtain effective lubrication with a fatty acid on copper, it was necessary to have both oxide and water vapour present. This would suggest that these conditions are necessary for soap formation.

H. Wilman: In connexion with the theory that friction of metals must be attributed to the formation and breaking of metallic welds at the junction regions of the sliding surfaces, I would like to know if Dr Menter would agree that this is unlikely to be the only source of friction; any process which causes a shear of parts of a crystal at

* Bowden, F. P., and Tabor, D. " Friction and Lubrication of Solid Surface."

† Tingle, E. D. *Nature, Lond.*, 1947, **160**, 710.

the surface over neighbouring parts will be opposed by forces due to the cohesion between the atoms across the plane of shear, thus contributing to the friction. Such opposing forces arising from local deformations of the contacting region contribute to the frictional force opposing motion, whether or not the two sliding metal surfaces are actually partly in metal-to-metal contact (welding). This will also be the case when two non-metallic (crystalline or amorphous) surfaces slide over each other, and presumably this resistance to shear and deformation must account for the observed friction of materials such as wood.

Recent work by my group, which is studying physical and chemical properties of surfaces in the Chemical Engineering Department at Imperial College, has shown by electron diffraction that unidirectional abrasion of a smooth metal single-crystal surface gives rise to a particular kind of disorientation of the surface regions. We find this is not a random disorientation but consists of a range of rotations of parts of the lattice about a well-defined axis which is usually not far from normal to the abrasion direction, but tends to be normal to a relatively densely-populated plane of atoms.* This is therefore evidence not only of the partial fragmentation of the crystal near the surface, but also of the shear of sheets of atoms over each other, probably in some cases by rotational slip,† in others by translational forms of slip.

In the case of an abraded iron crystal having a practically (110) face we have also observed that underneath the rotationally disorientated surface layer there is a layer of the face-centred cubic γ-phase of the metal in contact with the effectively undistorted underlying main α-iron crystal, and orientated in a definite epitaxial orientation relative to it. We showed that those observed orientations of γ-phase probably arise by a homogeneous shear of the α-crystal parallel to a (211) α plane, along the usual $\langle 111 \rangle$ type of slip direction, followed by slight contraction parallel to the $\langle 110 \rangle$ α direction, which lies parallel to these (211) α planes. This in turn raises the question of the effective temperature of the surface regions associated with the work done against the friction of two surfaces sliding over each other. Dr Bowden and his collaborators have indeed shown that the temperature may reach the melting point of the lower-melting material. In the above case of the iron, the γ-phase is normally only stable above 900° C, thus here the temperature may have exceeded 900° C, the γ-phase being, in effect, quenched by rapid conduction of the heat to the underlying mass of the specimen, so as to remain present at room temperature. In this dynamic aspect of the shear during frictional drag on a surface, however, there is concerned also the (probably relatively small) lowering of the transformation temperature as a result of the presence of the shear stress.

We are studying further the effects of surface shear, and also torsion, of crystals, particularly in connexion with a study of the process of wear.

F. P. Bowden and J. W. Menter: We agree that any shearing process occurring as a result of sliding one surface over another will result in the expenditure of energy, and so contribute to the observed friction.

B. E. Hurley: Partly with reference to Dr Cameron's remarks, what is the knowledge existing today about the viscosity of petroleum based lubricants: (1) under pressure of the same order as the yield of a hard steel, say 100 tons/sq. in.; (2) under the very high shear rates which must exist when two surface asperities pass at high relative velocity and small dimensional separation; (3) under a combination of both these conditions?

F. P. Bowden and J. W. Menter: Bridgman has shown that the viscosity of organic compounds increases with pressure. The effect is more pronounced with more complex molecules, particularly those containing long chains or side branches. Many substances with small molecules are solid at hydrostatic pressures of 5000 kg/mm², so that with the more complex molecules of lubricating oils one might expect these to be solid at even lower pressures. We do not know to what extent true hydrostatic conditions exist in practice. Clearly this will depend on both the micro- and macrogeometry of the surfaces. Our knowledge of changes in viscosity at high rates of shear is equally meagre, and it must be some time before the role of either of these parameters in fluid lubrication is clearly understood.

D. Summers-Smith: The theory of metallic friction proposed by Dr Bowden and his co-workers—the formation and shearing of the small junctions formed by welding of high spots on the opposing surfaces—is very familiar. This presents a satisfactory picture when one is dealing with metal pairs which form solid solutions or compounds with each other. However, very similar coefficients of friction are found between such diverse materials as plastics, wood, and ceramics and between combinations of them; thus one would expect a similar friction mechanism to be operating. It is less easy to visualize a "welding" phenomenon between these materials, and one wonders if the authors offer a similar hypothesis for the physical nature of friction between non-metallic materials and between metals and non-metallic materials. If so, have they any comments to offer on the nature of the junctions formed in these cases?

F. P. Bowden and J. W. Menter: During the past few years we have been making a study of the friction of non-metallic solids. With elastic solids such as diamond or rubber the area of contact is no longer proportional to the load, but to the two-third power of the load, since the deformation in the region of contact is primarily elastic. This means that Amonton's law no longer holds. There is evidence, however, that the friction is due primarily to adhesion at the interface. In the case of clean diamonds in a vacuum the shear strength in the region of contact is comparable with the bulk strength of diamond.‡ With plastic solids Amonton's law holds, and again there is clear evidence that local adhesion and welding occurs. Pascoe and Tabor have recently made a detailed investigation of the friction of "plastics."§ The results show that the deformation is neither purely elastic nor purely plastic, but is intermediate over a very wide range of loads.

Dr Atack of the Pulp and Paper Research Institute, Canada, who is working in our laboratory, is making a study of the frictional behaviour of wood. He has obtained some very interesting results, which show that there is a marked adhesion between wood and various sliders which is primarily due to hydrogen bonding. In addition to this the deformation of the wood is primarily elastic, and the rolling friction data may be interpreted in a manner analogous to that given for materials by Tabor;‖ that is to say, the rolling friction can be due primarily to elastic hysteresis losses within the material itself.

---

* Evans, D. M., Layton, D. N., and Wilman, H. *Proc. Roy. Soc.*, 1951, **A205**, 17; Agarwala, R. P., and Wilman, H. *J. Iron St. Inst.*, 1955, **179**, 124.

† Wilman, H. *Nature, Lond.*, 1950, **165**, 321; *Proc. Phys. Soc.*, 1951, **A64**, 329.

‡ Bowden, F. P., and Young, J. E. *Proc. Roy. Soc.*, **A208**, 444.

§ Pascoe, M. W., and Tabor, D. *Proc. Roy. Soc.* 1956, **A235**, 210–24.

‖ Tabor, D. *Proc. Roy. Soc.*, **A229**, 198.

HYDRODYNAMIC LUBRICATION AND ITS APPLICATION TO BEARING DESIGN *

By F. T. BARWELL †

SUMMARY

The results of experiments on fluid film lubricated bearings are usually expressed in the form of non-dimensional parameters. This is not always convenient for the designer as he has to separate the factors representing the duty to be fulfilled from those variables which are at his disposal as means to that end. It is shown that duty may be expressed in terms of a viscosity multiplied by a numerical factor whose magnitude depends on the dimensions and condition of operation of a bearing. This is referred to as the "Mechanical Viscosity" by analogy with "Mechanical Octane Number." The viscosity requirement of a bearing is discussed with reference to the limitation and potentialities of air as a lubricant.

The rational design of high-speed bearings is handicapped by lack of information regarding friction, amount of lubricant flowing, and temperature distribution. Work proceeding at the Mechanical Engineering Research Laboratory (MERL) to elucidate these factors is described, including an account of visual studies of lubricant film extent in transparent bearings.

The relationship between the contributions to be made by the petroleum technologist and the design engineer in meeting the demands of advanced mechanical engineering are discussed, and it is concluded that lubricants based on petroleum are likely to meet the main requirements during the foreseeable future.

NOTATION

E	Young's Modulus of Elasticity.	d	Diameter.
F	Force, frictional, tangential to motion.	e	Eccentricity.
I	Moment of Inertia.	g	Acceleration due to gravity.
L	Length.	h	Film thickness.
M	Mass.	h_{min}	Film thickness at closest approach.
N	Rotational speed.	k	Constant—defined in text.
P	Load per unit width.	p	Load per unit area.
R	Distance of centre of mass from centre of rotation.	p_f	Feed pressure.
T	Time.	r	Radius of journal.
U	Velocity—linear or peripheral.	ε	Eccentricity ratio, e/c.
V	Volume flow in unit time.	η	Viscosity.
W	Total load.	μ	Coefficient of friction.
b	Breadth of bearing, in direction perpendicular to relative motion.	ρ	Density.
c	Radial clearance.	ψ	Attitude angle of bearing.
		ω	Angular velocity.

INTRODUCTION

ALTHOUGH the phenomenon of hydrodynamic lubrication was discovered by Beauchamp Tower in 1885 and placed on a sound theoretical basis by Osborne Reynolds in 1886, a surprising number of engineers design bearings on what they refer to as a pV basis, p being load on projected area and V being the peripheral velocity (U in our notation). This expression might be some measure of a duty of a bearing in the absence of adequate lubrication, but because hydrodynamic lubrication becomes more effective the higher the relative speed of the sliding surfaces, the use of the expression is manifestly false as a basis for the design of well lubricated bearings.

Exponents of hydrodynamic lubrication theory express their results in the form of a parameter which they usually describe as ZN/P (in our units $\eta N/p$). Such an expression may describe completely the behaviour of a bearing, but is of little use to the designer because, whilst N will be fixed by the requirements, until he has proportioned the bearing he knows only the total load W and does not know what viscosity to introduce into the expression. $\eta N/p$ is a non-dimensional parameter, although its exponents seldom use consistent units. There appears to be a tendency to regard non-dimensional parameters as being particularly informative, and one sometimes suspects that terms are deliberately introduced in order to make a function non-dimensional. However, in other branches of design, the use of dimensional parameters has been useful. Moreover, for a design to proceed on a rational basis, it is necessary to separate means from ends. For example, in the design of light-weight structures, in particular aircraft, it is possible to define the problem by one set of coefficients (structure loading coefficients) and to characterize the means, in this case the properties of materials, by another set. Taking, for example, the characterization of a material to be embodied in a light-weight structure, the simplest property being tensile strength, one compares materials not on strength only or density only but on the basis of specific strength, *i.e.* ultimate tensile strength divided by density. This is a perfectly genuine criterion but it will be noted that it is not non-dimensional and has the dimension of length. Clearly, the units in which density and strength are measured must be consistent, and the

* MS received 3 February 1956.

† Mechanical Engineering Research Laboratory, DSIR, Lubrication and Wear Division, Thorntonhall.

result will be a definite length for each material irrespective of the units used, although it will be expressed in kilometres, miles, feet, or inches. Kilometres is preferable because it gives an easily handled number. A physical basis for the concept is provided by the fact that the specific strength is equal to the length of a uniform bar of the material which, hanging freely, will just break under its own weight. In the textile trade, for example, grams per denier is the measure of specific strength. The denier is the weight in grams of 9000 m of thread, and the weight at which the thread breaks is also measured in grams. It follows that specific strength expressed as grams per denier equals breaking load over the weight of 9000 m. Thus, 1 gram per denier equals 9 km. Specific strength in kilometres is therefore a useful number whereby materials can be characterized as means for doing a job. In this particular example, the job would be characterized by a single number representing load.

A more complicated duty, such as that to be performed by a strut, is defined by a slightly more complicated parameter. The design of a simple strut depends on the magnitude of the load and the distance through which this load has to be carried. Cox [1] has referred to this as the " structure loading coefficient," which in this case takes the form W/L^2.

Assuming the strut is long and slender so that failure occurs by buckling of the Euler type,

$$W = (\pi^2 EI)/L^2 \quad . \quad . \quad . \quad (1)$$

For a circular strut $I = (\pi d^4)/64$ where d is the diameter

$$\therefore \quad W = 0{\cdot}498Ed^4/L^2$$

If one considers another strut in which every dimension was increased n times the corresponding dimension of the original strut $W_n = (0{\cdot}489Ed^4n^4)/(L^2n^2) = n^2W$. However,

$$W_n/L_n^2 = (n^2W)/(n^2L^2) = W/L^2. \quad . \quad (2)$$

This has the dimensions of a stress.

Considering for the moment Euler type failure only, it will be noted that the weight of a strut would be proportional to ρd^2L so that the criterion for the efficiency of the material would be E/ρ^2. This would be the appropriate measure of the suitability of the material for construction of strut rather than the specific strength in kilometers previously mentioned.

Can one apply analogous principles to the design of bearings and the characterization of lubricants? If one can separate the definition of the duty the bearing has to perform from consideration of the means for fulfilling that duty, it may be possible to disentangle the elements of the $\eta N/P$ parameter for the convenience of the designers. The requirement of a bearing is always to carry a certain load W at a relative velocity U, the designer, however, is usually faced with other limitations. In a journal bearing, for example, the diameter of the shaft will already have been determined by strength considerations. One has therefore three factors, W total load, U translational velocity of the rubbing surfaces, and d some linear dimension characteristic of the scale factor imposed on the designer. The difficulty of the problem will be increased as the applied load is increased. Assuming hydrodynamic conditions, the difficulty will be diminished by increasing velocity, and it may be expected that the difficulty will be diminished as the scale of the bearing is increased. One therefore has W/Ud as a characterization property representing the requirement. Now the dimensions of this are $MLT^{-2}/(LT^{-1} \times L) = ML^{-1}T^{-1}$, which, it will be noted, are the dimensions of viscosity. This leads to the result, surprising to the engineer but no doubt commonplace to the petroleum technologist, that a measure of the difficulty of any lubrication requirement may be expressed in terms of viscosity.

Confining one's attention, for the purpose of illustration, to simply loaded complete journal bearings, one may use an expression for load-carrying capacity

$$W = \eta \frac{Ub^3}{4c^3} \frac{\pi\varepsilon}{(1-\varepsilon^2)^2} \sqrt{1 + 0{\cdot}621\varepsilon^2} \quad . \quad (3)$$

which is derived from a narrow bearing theory of Ocvirk.[2] This is approximate, and its limitations are referred to later. By regrouping the terms, one has

	Petroleum	Mechanical	
Customer	technologist	engineer	
W/Ud	$= \eta$	$\times (b/d)^3(r/c)^2 f(\varepsilon)$	. (4)

where the variation of $f(\varepsilon)$ with ε has been calculated and is plotted in Fig 1. The notation is explained in Fig 2. The expression may be divided into three portions—the left-hand side of the equation, which describes the customer's requirements, and the right-hand side divided into two portions, the viscosity, which is the concern of the petroleum technologist, and the dimensions and operating eccentricity, which are the concern of the design engineer. Following an analogy by Caris *et al*,[3] who talk of the " mechanical octane number " of an engine, one may speak of the term

$$(b/d)^3(r/c)^2 \frac{\pi\varepsilon}{(1-\varepsilon^2)^2} \sqrt{1 + 0{\cdot}621\varepsilon^2}$$

as being the " mechanical viscosity " of a bearing. So important is the relationship between the two partners represented by the factors of the right-hand side of the equation that the paper describes an examination of present-day knowledge of the mechanical viscosity primarily for the benefit of the other partner.

Considering an engine, the primary function of the piston is to seal the gas pressure whilst permitting work to be transmitted to the shaft. As regards the conditions between the piston and the cylinder wall, the factors to be taken into account are instantaneous gas pressure p, instantaneous piston speed U, and a factor governing the scale of the operation which for convenience can be taken as the cylinder diameter D. If one assumes hydrodynamic conditions the duty then

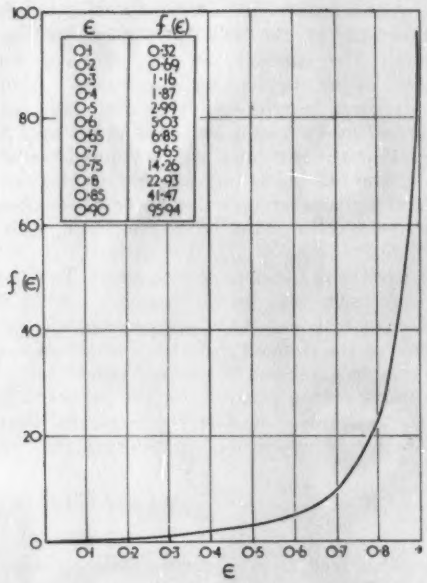

FIG 1

GRAPH OF $f(\varepsilon) = [\varepsilon\pi/(1-\varepsilon^2)^2]\sqrt{1+0{\cdot}0621\varepsilon^2}$ AGAINST ε

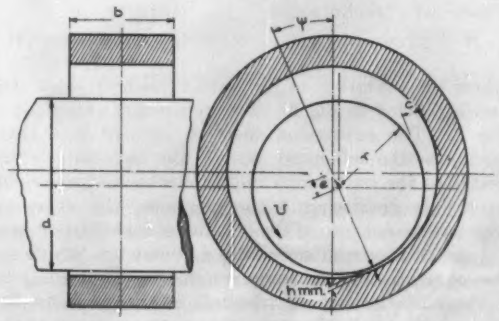

FIG 2

NOTATION

c = radial clearance. e = eccentricity. b = breadth of bearing. $e/c = \varepsilon$ = eccentricity ratio. $d = 2r$ = diameter of shaft. ϕ = attitude angle.

becomes $p \times D$ divided by U. This again has units equivalent to viscosity. One may therefore write an equation

Customer		Petroleum technologist		Design and Maintenance engineer
pD/U	=	η	×	factors governing efficiency of piston ring assembly . . (5)

It is a well known fact that when, due to wear, the mechanical factors to the right deteriorate it is necessary to compensate by increasing viscosity. Reverting to journal bearings and taking good modern practice as being represented by a b/d factor of $\frac{1}{4}$ and r/c of 1000 and operating at an eccentricity of 0·7,

$W/Ud = 0{\cdot}714\eta$ with W in lb, U in inches/sec, d in inches, and η in centipoises . . (6)

Thus a 1-inch bearing operating at 60,000 rev/min would carry a load of 6 lb if lubricated by air and 1375 lb if lubricated by oil of 5 cP viscosity. If, however, one was assured of perfect workmanship and increased r/c to 10,000 the load-carrying capacity with either lubricant would be increased 100 per cent, and it will be noted that the air bearing would be capable of carrying a substantial load.

The future of the air bearing therefore depends on the accuracy with which it can be produced. Research is therefore proceeding at the MERL to determine the practical limits of operation. Rotational speeds of 100,000 rev/min have been attained, but so far little success has been achieved in increasing load capacity to approach the 600-lb capacity indicated as being possible by the second example. It must be noted that one is discussing hydrodynamic or aerodynamic bearings, *i.e.* bearings which are self-sustaining in the absence of an external source of pressure. Air bearings which derive their film pressure from an external source are being used to an increasing extent, but their load carrying capacity is limited by the maximum supply pressure available.

MECHANICAL LIMITATIONS

Assuming for the moment the correctness of equations (3) and (6), consider the limitations imposed on the mechanical factor. First, one must consider that the bearing has to be manufactured. Neither the shaft nor the bearing will be the perfect cylinders envisaged by theory, neither will they be co-axial. Even if they were arranged to be co-axial when the machine was first assembled they would be unlikely to remain so when load was applied because of elastic deformation. It is therefore necessary to accept that the minimum film thickness must exceed a certain value so that none of the irregularities of the shaft shall contact the irregularities of the bearing and also that the average value used in design must exceed this minimum value to allow for relative, permanent, or transient misalignment of shaft and bearing. In the case of the air bearing in the second example given (clearance of 0·0001 and an eccentricity of 0·7) the average minimum film thickness will be 0·000033 inch. This is just under 1 μ, and it would be very difficult to ensure that foreign particles larger than this were not drawn into the bearing from the surrounding atmosphere. It is generally regarded as being the minimum film thickness for hydrodynamic lubrication.

Equation (6) is reasonably conservative. The results of carefully conducted laboratory tests indicate that failure occurs when the value of the parameter $\eta U/P\,(b/d)^2\,(r/c)^2$ is less than 0·015 (in consistent units). Failure, in a carefully controlled test, will

occur as eccentricity ratio approaches unity. The high value of the slope at the right-hand side of Fig 1 reveals the high overload capacity of a plain bearing provided the stringent geometrical requirements may be met. Thus, whilst under normal running conditions at moderate values of eccentricity, a new bearing will operate in exactly the same way as a well run-in bearing, the latter may be expected to be more resistant to extreme overloading.

For the conventional bearing ($b/d = \frac{1}{4}$, $c/r = 10^{-3}$) the expression corresponding to equation (6) for failure under laboratory conditions is

$$W/Ud = 4{\cdot}07\eta \quad . \quad . \quad . \quad . \quad (7)$$

Increase in the factor (b/d) has certain theoretical advantages, but in actual practice it is usually found best to restrict this value to a minimum so as to lessen the severity of the requirement for precise alignment. Modern high-speed bearings usually are best made very short because, owing to the high value of U, the overall viscosity requirement of the bearing is low, and it is sometimes economical to reduce the mechanical factor rather than the physical viscosity of the lubricant used. It is conceivable that it might be advantageous to increase the mechanical factor by increasing b but by reducing η by considerable factor. However, if one is to adhere to mineral lubricants the lowest viscosity mineral oil usually employed makes little demand on the mechanical factor, so that the shorter bearing is preferable for practical reasons. Minimum film thickness may be selected as the most important criterion rather than eccentricity ratio, or diametral clearance. The three factors are, however, related by the simple expression

$$h_{\min} = c(1 - \varepsilon) \quad . \quad . \quad . \quad (8)$$

If one is able to ascribe realistic figures to such factors as minimum film thickness it will be possible, using equations (3), (6), and (8), to derive optimum proportions for the bearing. As stated earlier, this would leave selection of viscosity as the main problem for the designer.

Equation (3) is derived from Reynolds' equation—

$$\frac{\partial}{\partial x}\left(h^3\frac{dp}{dx}\right) + \frac{\partial}{\partial z}\left(h^3\frac{dp}{dz}\right) = 6\eta U\frac{dh}{dx} \quad . \quad (9)$$

which has not been solved in a general way. Simplification has been made possible by the following assumptions, both of which involve a departure from an accurate description of the conditions in a bearing. First, the variation of velocity in the X direction attributable to pressure is neglected and, secondly, pressure is assumed to extend from point A to point B (Fig 10) around the bearing. However, the results for variation of eccentricity with load obtained from this theory have been shown by Ocvirk to be within reasonable agreement with experiments, and the equations have therefore been quoted as the only straightforward algebraic expressions available governing load-carrying capacity and friction of a bearing which accord with experimental results.

FRICTION

So far, however, only the minimum viscosity necessary to carry the load with given mechanical factors have been considered. Clearly some attention must be given to the frictional losses within a bearing. These are given approximately by the expressions

$$F = 2\pi\eta U b r/c \times \frac{1}{\sqrt{1-\varepsilon^2}}\left[1 + \tfrac{1}{4}(b/d)^2\frac{\varepsilon^2}{1-\varepsilon^2}\right] \quad (10)$$

or $$\mu = \frac{F}{W} =$$

$$2(d/b)^2(c/r)\sqrt{\frac{1-\varepsilon^2}{1+0{\cdot}621\varepsilon^2}}\left[1/\varepsilon - \varepsilon + \varepsilon/4(b/d)^2\right] \quad (11)$$

The variation of μ with ε is plotted in Fig 3. There is clearly scope for variation in the mechanical factor,

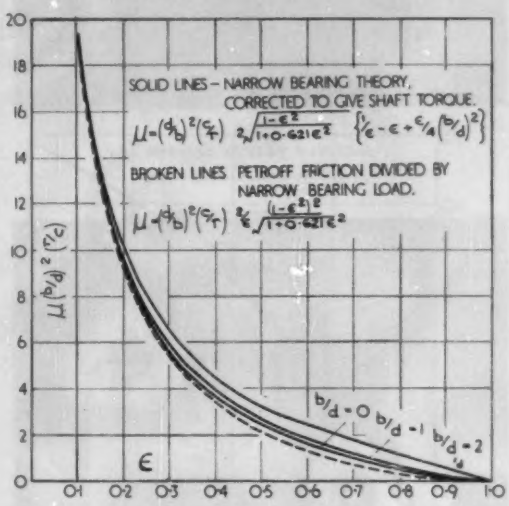

FIG 3

VARIATION OF COEFFICIENT OF FRICTION WITH ECCENTRICITY RATIO

advantage of which must be taken by using the minimum value of η. In practice this may vary from glass down to air, which at 100° C has a viscosity of 0·0218 cP.

The full curves on Fig 3 have been calculated by the narrow bearing theory for values of b/d of 2, 1, and 0. The dotted curve is based on a method frequently used in design. The friction torque is here calculated as though the bearing and shaft were concentric, by a method first suggested by Petroff.[4] The bearing is in fact treated as a rotational viscometer. The load carried is estimated for each eccentricity, in this case using the narrow bearing theory, and the coefficient of friction becomes Petroff Torque/($r \times W$). On first inspection of the curve, the lines

appear to be so nearly coincident that the differences between them do not appear to be important for practical purposes. However, if one is concerned with the higher values of eccentricity, coefficients of friction are low and the load capacity is large. The proportional differences are considerable, and this is

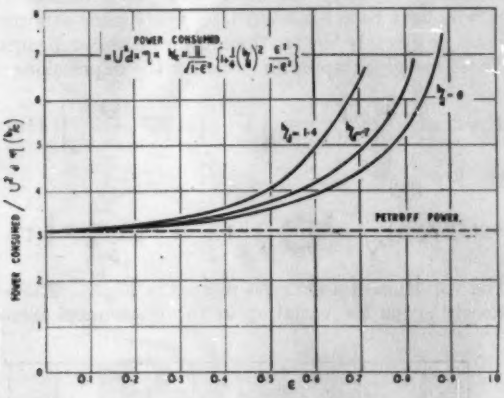

FIG 4

EFFECT OF ECCENTRICITY RATIO ON POWER CONSUMED

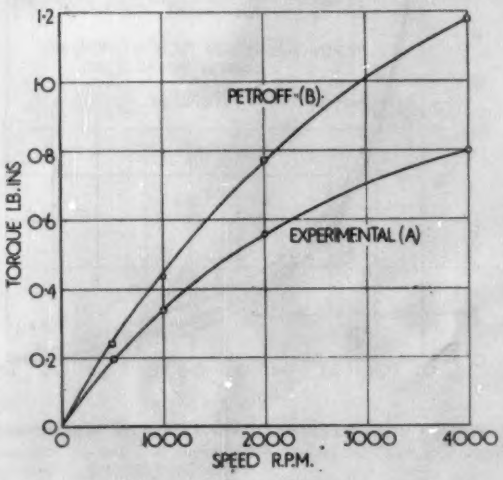

FIG 5

VARIATION OF BEARING TORQUE WITH SPEED

brought out more clearly in Fig 4, where power consumption is plotted against eccentricity ratio.

In the days of slow running machinery the important objective was that the bearing should carry the load with safety and with a moderately low coefficient of friction. Due to the low speed, the total power consumption was not of such importance that a 2 : 1 error in estimation was serious. Power loss goes up in proportion to U^2, so that the question assumes much greater importance when high speeds are involved.

Fig 5 shows the results of measurement of friction torque on a 1 inch dia bearing. The curve marked "Petroff" has been calculated using values for viscosity determined from the measured temperature of the bearing. It will be seen that the "Petroff" formula, Torque $= 2\pi\omega r^3 (b/c)\eta$, gives a seriously high result at high speeds. The discrepancy may be due to one or more of three factors, the effect of eccentricity, error in estimation of the effective viscosity, or incompleteness of the film.

FACTORS REQUIRED BY THE DESIGNER

It has been said that given a mechanical factor all that is necessary is to determine the viscosity of the lubricant. However, this provides the greatest difficulty to the engineering partner because the petroleum technologist partner provides lubricants whose viscosity varies so markedly with temperature. In fairness, one must acknowledge the achievement represented by the recent introduction of multi-viscous oils, but, even with these, the variation is very considerable. There can indeed be no sense of criticism of this feature because, as is shown later, the variation of viscosity with temperature may provide a self-adjusting mechanism which, coupled with the variation of eccentricity, does make the journal bearing into a virtually self-adjusting system. This explains why so many bearings have worked so successfully for so long although designed without serious regard for hydrodynamic theory. Indeed, it is only with the advent of the gas turbine and the new situation arising from the employment of very high rotational speeds that one feels justified in efforts to refine and extend hydrodynamic bearing theory.

In estimating the temperature of the oil film in a bearing, the first assumption made is that the heat generated in shearing the oil all goes to heat the oil, being carried away therewith by a convective process. This can be referred to as the adiabatic viewpoint which is to be contrasted with an isothermal process wherein heat is assumed to be conducted through the oil film to the surfaces of shaft and bearing shell. Undoubtedly such conduction takes place and will result in a lower temperature being reached than that given by the adiabatic assumption. It is the author's view, however, that a conservative estimate should be made based on the adiabatic theory. Two factors are therefore necessary to estimate the bearing temperature, the heat generated, namely friction of the bearing, and secondly, the amount of oil flowing through a bearing.

FRICTION

Equation (10) was based on the assumption that the bearing ran continuously full of oil of constant viscosity. Experimental determinations (Fig 5) show that the actual friction measured in a bearing at higher speeds falls below the value calculated on the assumption that the bearing was running full of oil of uniform viscosity being sheared uniformly around the bearing periphery. Very recent experiments at the MERL

throw light on to this question. Here transparent bearings are used and the lubricant illuminated by ultra-violet light.

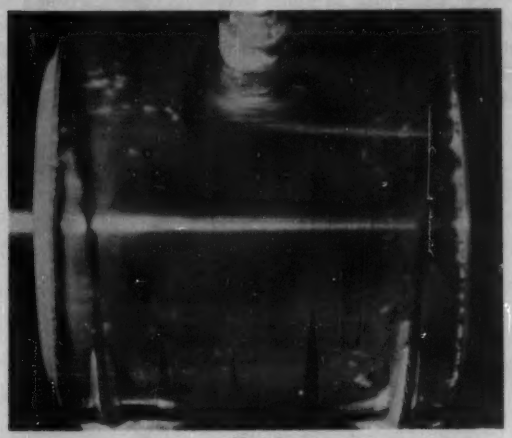

FIG 6

RUPTURE ON INLET FILM ONLY

Speed 1500 rev/min. Load 10 psi. Supply pressure 20 psi.

Glass tubes are used to represent the bearings, and load is applied by cables in order to obstruct the view of the bearing film to a minimum extent. In the cases illustrated, lubricant is supplied by a single hole, but other forms of entry have been explored.[5]

Under very light loads the film is almost continuous, as load is increased the portions of the film begin to rupture as shown in Fig 6. Increasing the load further, the film ruptures more completely, as shown

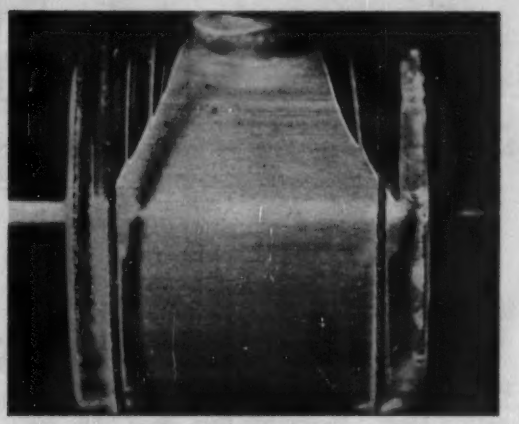

FIG 7

TYPICAL INLET PATTERN

100-lb load. 3000 rev/min. 6 psi oil supply pressure. Clearance ratio 0·00286.

in Fig 7. The oil issuing from the inlet hole spreads to cover the full width of the bearing after a considerable interval. The film is complete through the loaded region, and ruptures on the unloaded portion as shown in Fig 8. An interesting observation, which was unexpected by the present writer, is that when the film ruptures it forms fibrils of lubricant which extend through the unloaded region to rejoin the film in the inlet region. The effect of pressure has little effect on the position of the outlet film, but may have a considerable bearing on the position at which the film first forms. At low speeds and high supply pressures

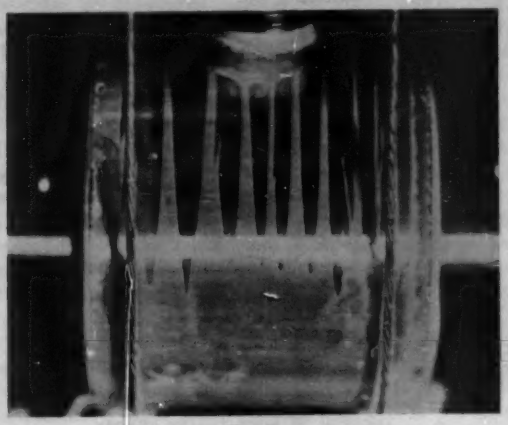

FIG 8

TYPICAL OUTLET PATTERN

Same conditions as Fig 7.

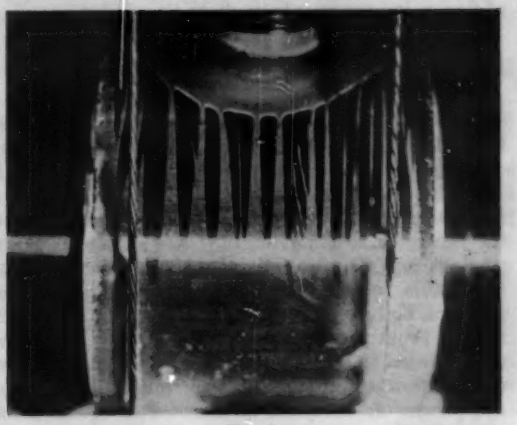

FIG 9

TYPICAL OUTLET PATTERN WITH "BACKWARD FLOW"

100-lb load, 3000 rev/min. 40 psi oil supply. Clearance ratio 0·00286.

it may even spread backwards from the inlet hole as indicated in Fig 9.

The use of this technique enables an assessment to be made of the validity of the assumptions regarding film extent in the simple theory. Here it was assumed that the pressure film extended from the point of maximum film thickness round to the point of minimum film thickness. Whilst visual studies do not indicate pressure, the lubricant may be present un-

pressurized. Where it is shown that there is no lubricant present one could be certain that no pressure is being exerted at this point. Fig 10 shows a comparison of results measured from the visual models with the assumption of the narrow bearing theory which is based on published data.[6]

It will have been noted that an important aspect of bearing design which is not taken into account in hydrodynamic theory is the behaviour of the lubricant

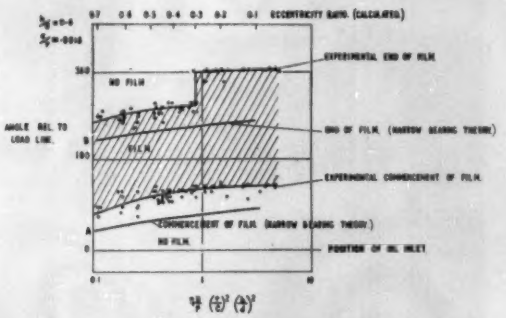

FIG 10

COMPARISON OF OBSERVED FILM EXTENT WITH THAT ASSUMED IN APPROXIMATE THEORY

in the unpressurized region. The visual technique may be of considerable value in exploring the effect of design improvements made in this region.

OIL FLOW

The narrow bearing theory gives the following expression for oil flow

$$V = Ucab \quad . \quad . \quad . \quad . \quad (12)$$

In this respect Ocvirk's experiments do not support the theory in so far as oil flow was shown to be dependent on oil pressure. In his report, however, he is able to employ a parameter embracing feed pressure, and he reports consistent behaviour on this basis. From the designer's point of view this curve may be used to estimate the pressure required to give normal flow conditions. If one takes the value of the parameter at which measured flow equals theoretical flow, one can estimate a pressure necessary to give theoretical flow. This may be expressed in the form of a simple equation as follows: Feed pressure required to obtain theoretical flow

$$p_f = k\eta\omega(r/c)^2(b/d)^2 \quad . \quad . \quad . \quad (13)$$

where $k = 1{\cdot}4$ for single-hole entry and 0·45 for axial inlet groove. This result must be regarded as an interim one and experiments at the MERL are still in process to provide more information. The accurate measurement of flow has been found to be a matter of great difficulty. The principle of the Marriot bottle (Fig 11) is being employed. Arrangements are being perfected whereby the rate of change in weight of the reservoir is used to provide a continuous record of oil consumption.

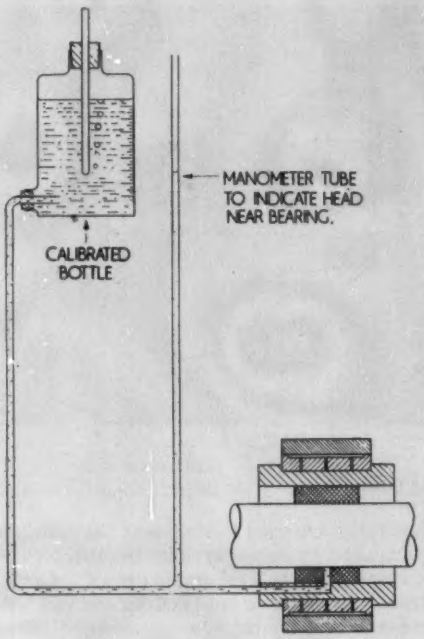

FIG 11

OIL FEED SYSTEM

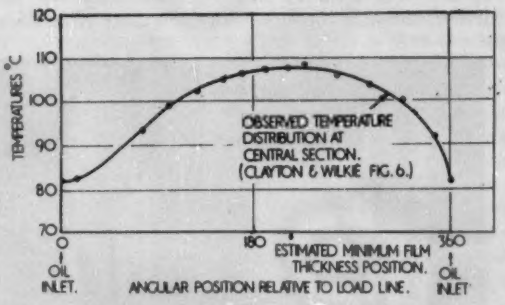

FIG 12

OIL FILM TEMPERATURE DERIVED FROM CLAYTON

THERMAL DISTRIBUTION

A simplified design procedure on the basis of the narrow bearing theory has been given,[7] but the following limitations will be apparent. All the previous theory has been based on the assumption that viscosity is constant throughout the oil film. It is clear, however, that if temperature is varying, viscosity is varying also. The writer believes that a rational design procedure may be based on selection of the appropriate average value. However, it is clear that one would be in a better position if one knew in fact

how temperature varies throughout the oil film. Fig 12 shows the results of some experiments by Clayton at the NPL wherein temperatures near to the surface of a bearing were measured using an array of thermocouples. The preliminary result shows temperature to be a maximum near the point of minimum film thickness and to fall off beyond this. Clearly, if all the heat were convected away within the oil this would not occur. Fig 13 shows the apparatus in use at the MERL in an extension of this work to high-speed bearings.

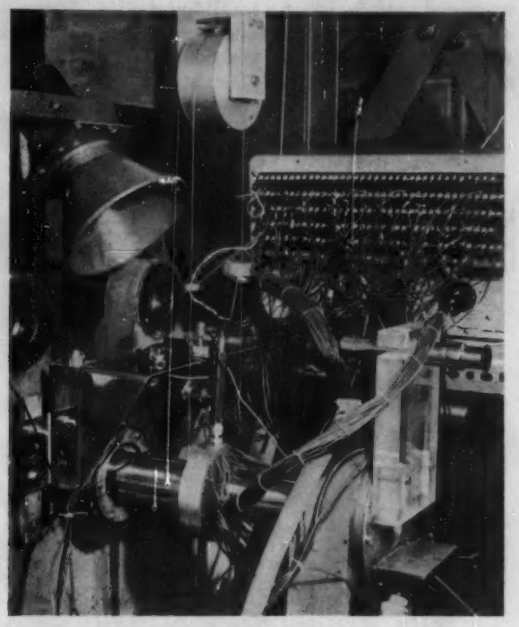

FIG 13
APPARATUS FOR STUDYING TEMPERATURE DISTRIBUTION IN COMPLETE JOURNAL BEARINGS

THE BEARING AS A SELF-ADJUSTING SYSTEM

It has been noted that the load-carrying capacity of a bearing depends on the viscosity of the lubricant. This depends on the temperature, which in turn depends on the frictional heat generated in a bearing and the amount of lubricant passing.

Consider a bearing operating under steady load at a moderate value of eccentricity ratio. If the load is increased, the eccentricity ratio will be increased also, and the frictional heat will increase moderately as indicated by Figs 3 and 4. However, because of the operation of equation (12) the amount of lubricant flowing will increase in direct proportion to the increase in eccentricity ratio. Because rate of lubricant flow increases more rapidly with eccentricity ratio than heat generation, a new equilibrium will rapidly be reached.

Consider an increase in speed. The first effect would be to reduce eccentricity ratio. Lubricant flow would be increased by an amount proportional to speed increase and reduced in proportion to reduced eccentricity ratio. Frictional heating would be increased as the square of the speed, again slightly modified by change in eccentricity ratio. It is clear, however, that, due to the operation of the square law, the extra heat generated as a result of an increase in speed will exceed proportionately the extra lubricant drawn through the bearing. Temperature will therefore rise, bringing in its train a reduction in viscosity. This will have two effects, one a reduction in frictional heat generation and two an increase in eccentricity ratio with consequent increased oil flow. These two effects will result in a new equilibrium with the bearing operating at an increased temperature. Indeed, some investigators have found it almost impossible to vary the value of the parameter $\eta N/p$ by varying speed.

A truly iso-viscous oil would not behave in this manner and, whilst its advent would greatly simplify bearing calculations, it might prove to be a grave embarrassment when bearings were required in practice to operate under a different condition from those assumed at the design stage.

BEARINGS UNDER VARIABLE LOADING

Whilst there is a tendency for research workers to concentrate on bearings under steady load as a matter of convenience, it is clear that in practice loading conditions vary widely. General hydrodynamic principles are the same, however, and if, for example, one assumes that the applied load will rotate at a frequency different from the speed of rotation of the shaft, hydrodynamic theory reveals an equivalent load capacity as given by the steady load capacity multiplied by

$$(1 - 2N_d)/N \quad . \quad . \quad . \quad . \quad (14)$$

where N_d is the speed of rotation of the load. An important case with high-speed machinery occurs when the load arises from the action of centrifugal force. Whilst no doubt the greatest care is taken with balancing of high-speed machinery, this can never be perfect, for, even if a turbine rotor is perfectly balanced when cold, it may be expected to distort slightly during heating or cooling, with consequent out of balance. The seriousness from the situation is illustrated in Fig 14, where it will be noted that the geometric perfection of balance required for high-speed rotor for the bearing load due to centrifugal force not to exceed the steady load due to the weight of the rotor is very great indeed. Various aspects of this matter are being explored at the MERL, and in one instance a machine has been constructed to operate up to speeds of 100,000 rev/min. From the

design point of view, relation of equation (4) with equation (14) is all that is necessary to determine the effective viscosity requirements.

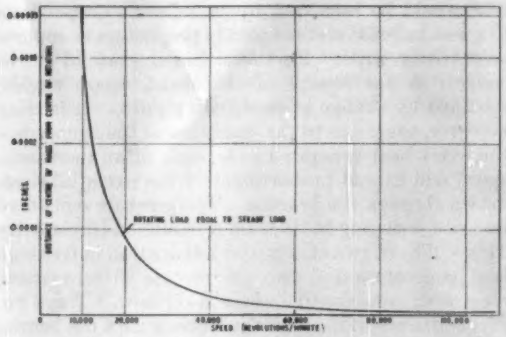

FIG 14

EFFECT OF UNBALANCE ON BEARING LOAD

Thus, if one considers the effect of a known amount of unbalance which may be expressed as the rotor mass times distance R, then, if ω is the rotational speed, centrifugal force $= (W/g)\omega^2 R$, $\omega = 2U/d$, so that the total duty of the bearing may be expressed as $\left(W + \frac{W}{g}\omega^2 R\right)/Ud$.

For high speeds it appears from Fig 14 to be justifiable to neglect the first term, then the duty becomes $= 2(W/g)\omega R/d^2$ or $WU \times (4R/gd^3)$.

This again has the dimensions of a viscosity, but, in contrast to the situation where the load on the bearing is applied by an external agency and is constant, for a given rotor in a given state of unbalance, viscosity requirement increases with speed. This factor is likely to militate against the use of air in larger high-speed machines.

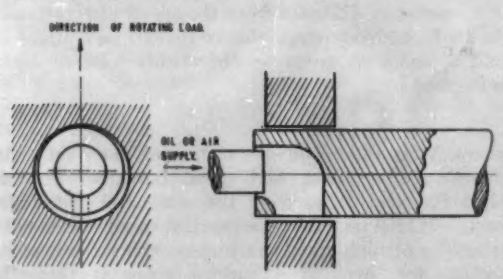

FIG 15

METHOD OF SUPPLY OF LUBRICANT WHEN LOAD ROTATES

Further work is necessary to determine the lubricant flow in bearings subject to rotating load. In contrast to the steady loading case, where the low-pressure region is stationary and provides a convenient location for the introduction of lubricant, when load rotates, the low-pressure region rotates in consonance therewith. Therefore, if oil entry ports are placed in the stationary bearing shell, they will be repeatedly subjected to a high internal or back pressure. Their presence may result in a serious local weakening of the pressure film and, unless very high feed pressures are employed, it is difficult to visualize an adequate flow of oil through the bearing. The alternative is to supply oil through the interior of the shaft. The position of the outlet ports is likely to be critical, however, and cannot be determined until the angular sense of the shaft unbalance has been located. It is suggested therefore that a small but definite degree of unbalance be designed into the rotor and ports provided in the corresponding position. Such an arrangement is illustrated in Fig 15.

BEARING OSCILLATIONS

It is well known that in unfavourable circumstances bearings can reveal oscillatory phenomena sometimes leading to failure. If one refers to equation (14) it will be seen that if a frequency of load application is half

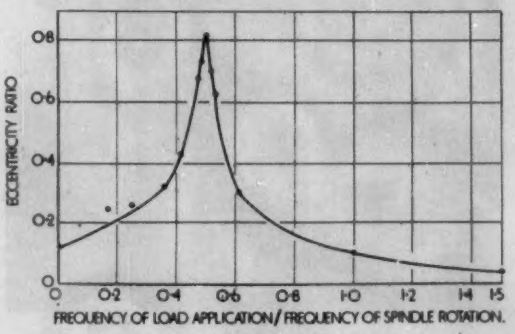

FIG 16

EFFECT OF FREQUENCY OF APPLIED LOAD

the shaft speed the load-carrying capacity is zero. Dayton and Simons' experiments [8] (Fig 16), in which an alternating load was applied to a rotating journal, confirm that equation (14) is applicable to alternating loads. If this is regarded as a forced vibration one would expect half shaft speed to correspond with the resonance in an elastic system, and therefore a self-excited vibration might occur at this frequency. Observations at the MERL indicate that self-excited vibrations of this character occur only under conditions of full film, and if the film is broken the vibration ceases. Another possible form of vibration arises from the interaction between the mechanical vibration of the components carried by the bearings and the bearing itself. When the frequency of an alternating load is less than half the shaft speed the bearing leads, as is confirmed by the experiments of Shawki and Freeman,[9] again using alternating load. Their results are summarized in Fig 17. Clearly this leading component will provide a forcing effect on any natural vibration of the shaft, and Newkirk has shown that when the natural frequency of transverse vibration of

the rotor is less than half shaft speed, the vibration is likely to be a problem. It would appear from Newkirk's results that the risk of vibration is reduced by working at high eccentricities, and work at the MERL is planned with the object of defining the limits of safe operation.

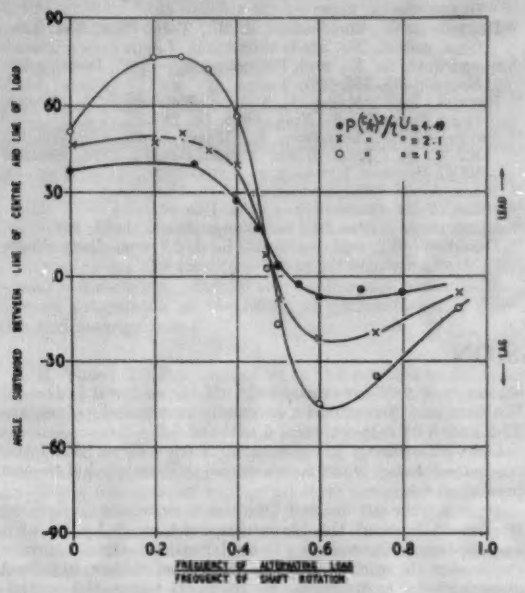

FIG 17

PHASE CHANGES UNDER ALTERNATING LOAD

CONCLUSIONS

The journal bearing has been taken as an example of hydrodynamic lubrication. The thrust bearing presents similar problems, and the parameter W/Ud is equally applicable. The Michell tilting pad bearing provides an almost perfect solution to the thrust bearing problem, but again where speeds are high and loads comparatively light the frictional losses may become excessive. Work is going on therefore at the MERL to explore what modifications may be desirable in design to provide a more acceptable solution to the problem of carrying comparatively light thrust loads at very high speeds.

Oscillating bearings represent a considerable problem because the parameter W/Ud clearly reaches infinity instantaneously at the point of reversal of motion. However, it has been shown [10] that in favourable circumstances hydrodynamic conditions operate even when W is maintained at a constant positive magnitude.

When lubrication of concentrated contacts such as those encountered in gears is under consideration, the duty required of the lubricant becomes very much more severe than in the case of journal bearings. Here again, hydrodynamic conditions are possible, but the local pressures reached may be so intense as to cause viscosity of the lubricant to attain a high value and to cause a local deformation of the contacting surfaces. A complete theory of this situation would require a study of the hydrodynamic conditions in a film the shape of which was modified by this elastic deformation, indeed a formidable mathematical problem. The term elasto-hydrodynamic lubrication has been applied to this condition, and it is to this region that the attention of theoreticians is likely to be directed in the immediate future.

When the parameter W/Ud indicates a combined viscosity and design factor beyond the range of technical possibility, for example when very high loads have to be carried at very low speeds, hydrodynamic theory ceases to be of great assistance to designers, and they may well in these circumstances fall back on the pU criterion. However, it has been shown [11] that hydrodynamic behaviour may extend to conditions where there is complete absence of wedge action and where the local irregularities of the surface may be expected to enter into the problem. This region of lubrication is known alternatively as " mixed lubrication " or " thin film lubrication," and remains an interesting field of study.

Finally, where conditions are so severe that hydrodynamic lubrication cannot exist, boundary lubricants have to be considered. Development of such materials as PTFE or molybdenum disulphide bonded to a phosphated surface will enable loads to be carried satisfactorily, although in these circumstances a certain amount of wear may be unavoidable.[12]

Further, no mention has been made of grease, another petroleum product entering into lubrication. It has been shown [13,14] that hydrodynamic theory may be modified to take into account the peculiar rheological properties of such materials. Theoretical treatments have been published, and work is proceeding at the MERL to elucidate the effects of the structure and the rheological properties of the grease on its performance in bearings.

It is now customary to speak of a lubricant as being multi-functioned.[15] In addition to separating moving surfaces, it should protect them against corrosion and should carry in suspension products of combustion and so forth. This should not, however, make one lose sight of the unique position held by petroleum-base lubricants in respect to the separation of the surfaces which the present writer regards as being their primary function. It would be possible, using water for example, to incorporate additives, corrosion inhibitors —sodium nitrite for example—alkaline materials to neutralize acids arising from products of combustion, and detergents for dispersing carbon particles. Indeed, water would probably be a much more effective solvent for additives than petroleum. However, the operating temperature range is limited by freezing at 0° C and boiling at 100° C, and the product is available in only one viscosity. Petroleum based lubricants have the advantage of a low pour point and stability at higher temperatures than 100° C. They are available in a wide range of viscosities, and their

change of viscosity with temperature is not the unmixed disadvantage sometimes assumed because, as discussed earlier, it provides an automatic measure of adjustment of the effective viscosity to operating conditions. Whilst applications exist in mechanical engineering for air, water, glass, and even liquid metals as lubricants, and whilst synthetic materials may have advantages over petroleum products in extremely severe applications, there is little doubt that petroleum will remain the major basis for the production of lubricants, and any study based on its application will be of lasting value.

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DISCUSSION

A. Cameron: The safety of a bearing depends on the minimum film thickness, and hence on the eccentricity ratio. The limit method of design, as typified in the author's analogy of the buckling load of a strut, therefore requires a maximum limiting value of eccentricity ratio.

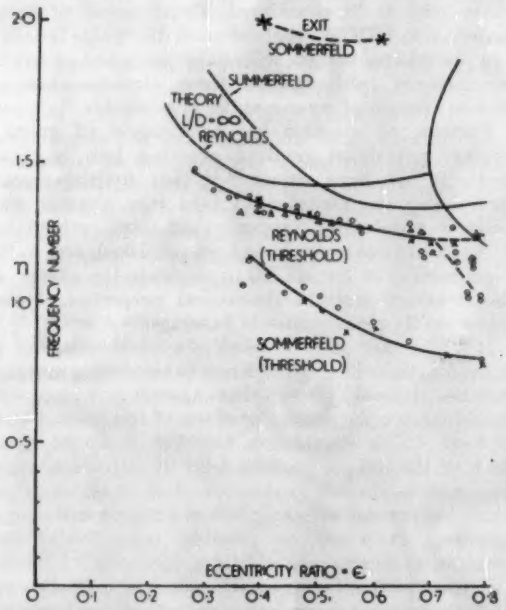

FIG A

Ockvirk's approximate treatment can apply only when the circumferential pressure gradient dp/dx or $dp/Rd\theta$ is small compared with the axial gradient dp/dy. This does not obtain at high values of eccentricity, where the limit design figures are required.

This is shown if the values of the Sommerfeld variable at, say, $\varepsilon = 0{\cdot}95$ are compared for $L/D = 1$ and $L/D = \frac{1}{4}$ Walther and Sassenfeld's acurately computed values are 37·2 and 5·08 respectively, a ratio of 7·3.

Ockvirk's theory gives a ratio of 64. Even at 0·7 the computed ratio is 28·2, which is still much below the predicted 64.

It is a pity to extend Ockvirk's excellent simplified treatment beyond the limits imposed on it by its own assumption. Considering the friction, the accurate expression is surely simpler than the rather involved approximate expression, as in both cases the eccentricity ratio is needed anyway.

The limits of Ockvirk's theory are also shown in equation (12), which states $V = U\varepsilon b$, the accurate theory shown that $V \longrightarrow 0$ as $\varepsilon \longrightarrow 1$.

It is most important to define very clearly the limits of Ockvirk's simplified theory, especially when limiting performance is being discussed.

We have been doing some work on vibration of bearings (oil whirl) and have found that the phenomena can be observed when the oil film is either continuous or discontinuous, *i.e.* under condition of Reynolds or Sommerfeld. Our apparatus has clearance of $\frac{1}{4}$ inch, but has been scaled to give a Sommerfeld number of the same order as that found in normal bearings. The figure is self-explanatory. An interesting feature is that the whirl is found to be a flatly "tuned" vibration, and at high speeds it is possible to get beyond the resonance into smooth running conditions. The ratio vibration–shaft frequency varies with ε and is between about 0·46 and 0·6.

E. S. Sellers: In Dr Barwell's equation (4), it is important to remember that his "mechanical viscosity term" is not independent of viscosity. In general, the eccentricity ratio, ε, is some function of $\frac{Pc^2}{\eta U r^2}$, so that for a given bearing with fixed speed, a change of viscosity changes ε as well as W. The variation of ε with the other terms is given in equation (4), where $f(\varepsilon) = \left[\frac{W}{Ud} \cdot \frac{1}{\eta} \cdot \left(\frac{d}{b}\right)^2 \left(\frac{c}{r}\right)^2\right] = \left[\frac{P}{\eta U} \cdot \left(\frac{d}{b}\right)^2 \left(\frac{c}{r}\right)^2\right]$, and the value of the latter group may be substituted for $f(\varepsilon)$ as the ordinate of the graph of Fig 1.

It is perhaps not sufficiently emphasized that the comparisons of air and oil using equation (6) are made

at the same arbitrary eccentricity ratio of 0·7. It is understood from p. 307 that 0·7 is a safe value.

If we may use ε as a criterion for maximum load allowable with a given viscosity oil, this will give h_{min} from equation (8), and this will be most useful in specifying the maximum particle size which can be passed by a filter.

In regard to oil flow, does equation (12), $V = Ucsb$ fit the facts? This implies that with a concentric shaft, $\varepsilon = 0$ and $V = 0$. With the shaft touching the bearing $\varepsilon = 1$ and V is a maximum.

Equation (12) represents the flow of oil leaking out of the bearing. It is likely that the cooling effect of the oil is related also to the circulation inside the bearing.

The ordinary theory of journal bearings gives, for circumferential flow between journal and sleeve, the volume flow rate/unit width, $V/b = Uc\left(\frac{1-\varepsilon^2}{2+\varepsilon^2}\right)$, *i.e.* when $\varepsilon = 0$, $V = \frac{1}{2}Uc$, and when $\varepsilon = 1$ (surfaces touching) $V/b = 0$. Over the range of $\varepsilon = 0{\cdot}5 - 1{\cdot}0$, a reasonable approximation is $V/b = Uc \cdot \frac{3}{4}(1-\varepsilon)$. The effect of eccentricity on the two flow rates is then seen to be in opposite directions. Could the author say what is the relative magnitude of the effect of circumferential flow rate and leakage rate?

J. K. Vose: Dr Barwell refers to the marked reduction of bearing temperature found when the delivery pressure to the transparent test bearing, which is illustrated, is increased until a sensibly full inlet oil film is obtained. Would the author give his opinion as to whether these lower temperatures are associated with lower losses or are only a function of higher oil flow through the bearing and, perhaps, better heat flow to the oil owing to higher turbulence in the exit region?

Dr Barwell spoke of the self-regulating nature of the mechanism of lubrication. I should like to ask him whether it would be correct to assume that in two bearings of similar dimensions (dictated by the machine to which they are fitted), but one ring-oiled and the other fed with oil at a sufficient pressure to flood the inlet area of the bearing, that which is ring-oiled would prove to be the more efficient, even when the power to drive the oil pump is neglected.

F. T. Barwell: I would like to re-emphasize the main point of the paper, namely, that having isolated the "mechanical factor," our knowledge thereof is still insufficient in the quantitative sense, so further research is justified.

In order to make progress it is necessary to select from available information, and when, as in the present paper, one desires to examine qualitatively the effect of different variables, a treatment such as Ocvirk's, which yielded results in algebraic terms, is preferable to that of Sassenfeld and Walther, wherein each condition had to be evaluated numerically. Dr Cameron referred to the Sassenfeld and Walther results as being "accurate" in contrast to Ocvirk's "simplified" treatment. It is true that the assumptions of Ocvirk's theory are somewhat drastic and that its results are only applicable to narrow bearings. However, the so-called "accurate" treatment also contains drastic assumptions. For example, it was assumed that the pressure-carrying film started at the point of commencement of convergence and terminated when $dp/d\phi = p = 0$, there being no negative pressure or discontinuity at the point of film breakdown. Neither of these assumptions would appear to be justified from consideration of the film shown at the meeting.

Nevertheless, the two theories were in agreement for the case when $b/d = \frac{1}{4}$. For a given Sommerfeld number the Ocvirk theory gives about 3 per cent lower eccentricity than Sassenfeld and Walther for $b/d = \frac{1}{4}$, about 10 per cent lower for $b/d = \frac{1}{2}$, and 20 per cent lower for $b/d = 1$.

As regards oil flow, it is apparent both from Professor Sellers' and Dr Cameron's remarks that the paper does not make it sufficiently clear that equation (12) refers to the oil flowing through and out of the bearing and not to that circulating within the bearing. In the hypothetical case when eccentricity ratio was unity, all the lubricant which filled the clearance space had to be expelled from the bearing so that flow would be expected to be large and not to approach zero as Dr Cameron suggests. Experimental results show that flow can be divided into two components, that due to feed pressure, and that due to hydrodynamic action. The latter component is less than predicted by equation (12) and, at present, equation (13) is the best guide available for design purposes.

In regard to Dr Cameron's experiments on vibration of bearings, it is not quite clear what he means when he refers to Reynolds and Sommerfeld conditions. Although a film might be continuous, this does not imply that the negative pressures envisaged by Sommerfeld exist. Circulation might take place in the unloaded region, the lubricant remaining substantially at atmospheric pressure. Again, whilst the figure is stated to be self-explanatory, the term "frequency number" is not defined. Although there appears to be no theoretical reason why bearing vibration should not occur when the film was discontinuous, the self-existed vibrations, which are usually referred to as "half speed whirl," have only been observed at MERL when the film was continuous.

In reply to Professor Sellers, it is true that eccentricity ratio is governed uniquely by the extended Sommerfeld number $P/\eta U(d/b)^2(c/r)^2$ and that this is numerically equal to our $f(\varepsilon)$. The rearrangement of terms suggested in the paper does, however, enable the "mechanical factor" to be regarded as a purely geometrical concept, which in association with lubricant of definite viscosity, enables a certain load to be carried. If load applied and load capacity do not balance and viscosity remains constant, eccentricity will change so as to adjust the mechanical factor. If load remains constant and viscosity changes, adjustment of eccentricity will occur to restore equilibrium. In this sense only is the mechanical viscosity dependent on viscosity.

Any cooling effect provided by the oil circulating within a bearing is neglected in the paper. Further research of the type illustrated in Fig 13 is required to fully elucidate the point. As an interim answer one can state that only the oil which left the bearing conveyed away an appreciable amount of heat, but that, for this to occur, this oil must pass some way around the periphery of the bearing. Merely increasing side flow by increase in lubricant supply pressure results in oil leaving the side of the bearing in the vicinity of the supply point without making an effective contribution to the cooling of the bearing.

In reply to J. K. Vose, lower temperatures resulting from increased delivery pressure are associated with higher oil flow rather than reduced losses.

Provided the conditions of speed and load were not too onerous, one can expect the ring-oiled bearing to be more efficient, if not more reliable, than the externally-fed bearing.

THE FRICTIONAL PROPERTIES OF MOLYBDENUM DISULPHIDE*

By J. W. MIDGLEY, M.Sc., D.I.C.†

SUMMARY

From experiments conducted on unbonded natural molybdenum disulphide films, it is found that the frictional resistance of such films decreases with increased dryness of the film. The results of other authors are shown to be in agreement with this conclusion, which also accounts for those obtained on bonded molybdenum disulphide. The practical significance of the results is discussed, and the results are compared with the known characteristics of graphite.

INTRODUCTION

RUBBING molybdenum disulphide films results in the orientation of the molybdenum disulphide crystallite cleavage planes parallel to the rubbing plane,‡ in the same way as occurs in graphite.[3-6] Until recently, this has been a satisfactory and sufficient explanation of the well-known excellent lubricating properties of molybdenum disulphide films. However, a number of different observers, particularly Peterson and Johnson,[9,10] have now observed that these lubricating properties are significantly dependent on temperature and humidity. They concluded [10, page 7] that the decrease in μ with increase in temperature, observed at room humidity, is a function of decreased metallic contact resulting from the better adhesion of the molybdenum disulphide to the steel substrate, as adsorbed moisture is desorbed from the steel with rise in temperature.

It appears to the present writer that another, more acceptable, interpretation of their results is that μ decreases with increasing dryness of the molybdenum disulphide film. It is shown that this possibility appears to provide an adequate and more logical explanation of all the important features of Peterson and Johnson's results [9,10] on both bonded and unbonded molybdenum disulphide films, and could account for the hitherto unexplained results of Johnson, Godfrey, and Bisson,[7] who observed a decrease of μ with increased sliding velocity for bonded molybdenum disulphide, and Barwell and Milne,[1] who found that the frictional resistance decreased with increase in load. This theory is confirmed by the following investigation, which has been made on molybdenum disulphide films, of sufficient thickness that the complicating factor of intermetallic contact does not arise.

EXPERIMENTAL DETAILS

Experiments were made using the best quality natural molybdenite powder, processed by Murex Co. Ltd.

The powder would not adhere when it was applied dry to the mild-steel annuli which it was intended to lubricate. However, when applied in an ethyl alcohol suspension, which was allowed to dry *in situ*, the adherence was quite good. This method was therefore adopted in the present investigation. The resin-bonding method of Johnson, Godfrey, and Bisson,[7] while of proved practical importance, was not employed in the present investigation, as the object was to study the behaviour of molybdenum disulphide, and the presence of burnt-off resin, which is associated with their method, would have introduced unknown secondary effects which would have been difficult to evaluate.

Thick films of the powder were applied, from ethyl alcohol suspension, to the bearing interface of pairs of degreased lathe-turned mild-steel annuli of 0·93 cm width and mean diameter of 7·14 cm. The molybdenum disulphide films were made approximately 0·5 mm thick, so as to eliminate the possibility of intermetallic contact between the two annuli. The annuli were then pressed together under a load of 85 kg, a nominal pressure of 4 kg/cm^2 (60 p.s.i. approx) and, with the top annulus restrained from rotation, the lower of the pair was rotated at a constant mean interfacial speed of 28 cm/sec (56 ft/min). The friction and wear machine used was developed, and kindly lent to us, by the Mechanical Engineering Research Laboratory, Lubrication and Wear Division, DSIR. In this machine the friction is measured, and continuously recorded, by the effect of the frictional torque on the capacitance of three spring-loaded condensers. The atmosphere surrounding the specimens can be controlled, and the present experiments were conducted in air at room humidity, the humidity of which was measured by a wet and dry bulb hygrometer, and also in an atmosphere of air dried by concentrated sulphuric acid and liquid nitrogen, giving a relative humidity of less than 0·1 per cent. The temperature was measured by a thermocouple embedded in the top annulus, 0·2 mm from the rubbing surface.

RESULTS

An optical and electron microscopic study was made of the powder. This showed that the particle diameters were in the range 1–3 μ, with some of the order of 10 μ which may be aggregates of the smaller particles. Fig 1 well illustrates the plate-like characteristics of the particles. As will be seen, the edges of

* MS received 25 January 1956.

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‡ Thirsk, H. R. (1938), unpublished work in this laboratory.

the particles are semi-transparent to the electron beam and are therefore 500–1000 Å thick, much thinner than the body of the particles. This "edge appearance" is characteristic of graphite as well as molybdenum disulphide powders, and arises from the overlapping of the crystal laminations at the edge, the laminar sheets being approximately in the plane of the figure. The hexagonal platelet near the centre of the figure shows the laminar structure particularly well, it is approximately 1·5 μ dia and 0·05–0·1 μ thick, a thickness/diameter ratio of 1 : 20. This ratio was also found to be typical of most of the particles measured and accounts for the ease of orientation of the laminæ, facilitated by rubbing, with the resultant low frictional resistance.

The moisture content of the powder, when in equilibrium with an atmosphere of 60 per cent room humidity (R.H.), was determined by drying in an air-oven at 120° C, and found to be 1·1 per cent.

It was found that thick films of this powder exhibited a relatively high initial coefficient of friction, $\mu = 0{\cdot}2$. On running the molybdenum disulphide lubricated surfaces together at room humidity (55–65 per cent R.H.), the frictional resistance steadily decreased to $\mu = 0{\cdot}05$ in ½–3 hr; the temperature of the upper mild-steel annulus rising from 22° to 50° C.

Experiments were then made to determine whether the observed reduction in frictional resistance on rubbing was primarily facilitated by the frictional heating, or by the resulting drying of the film.

It was found that, if the rubbing was stopped and the surface allowed to cool to room temperature in a dry atmosphere (<0·1 per cent R.H.), then the low frictional resistance ($\mu = 0{\cdot}05_5$) was maintained, but,

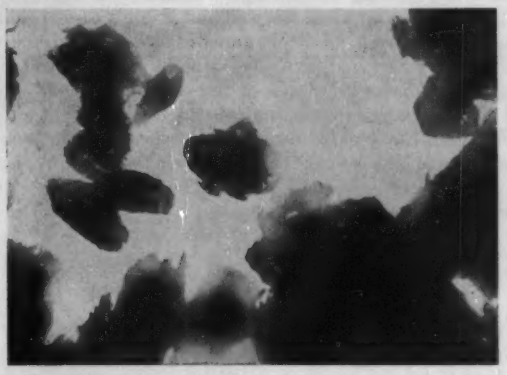

FIG 1

AN ELECTRON MICROGRAPH OF THE MoS_2 POWDER SHOWING THE LAMINAR STRUCTURE (× 9000 IN ORIGINAL)

if the cooling took place at room humidity, then the frictional resistance trebled, to $\mu = 0{\cdot}15$. These results, which have been confirmed by a series of experiments, clearly show that the observed reduction in frictional resistance with rubbing time was largely controlled by the moisture content of the film. In other experiments, the effect of supplying heat, in addition to that generated frictionally, was evaluated. The graph (Fig 2) shows a typical run made on a natural molybdenite powder film at room humidity; the above results are also shown on the graph. It will be seen that frictional heating and rubbing reduced the coefficient of friction from an initial value of $0{\cdot}19_5$ at 22° C, to $0{\cdot}09_1$ at 50° C,

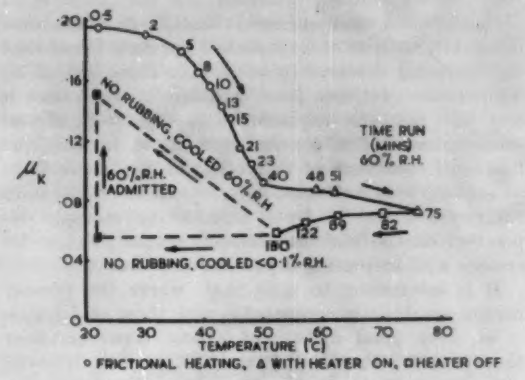

FIG 2

μ v TEMPERATURE FOR NATURAL MoS_2-LUBRICATED MILD STEEL

in 40 minutes; subsidiary heating to 76° C resulted in a further decrease to $\mu = 0{\cdot}07_1$ after 75 minutes, but when this heater was turned off and the temperature fell, as shown, to 52° C after a total of 180

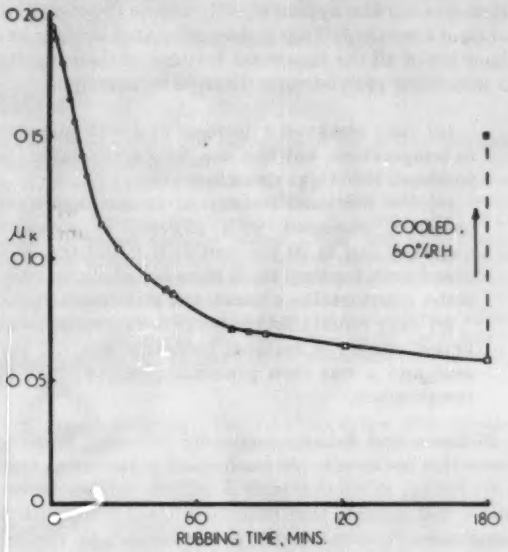

FIG 3

minutes, the frictional resistance continued to fall, to $\mu = 0{\cdot}05_8$. Fig 3 shows the same results plotted with the friction as a function of rubbing time. As will be seen, the friction at room humidity uniformly decreased with rubbing time; the small amount of

subsidiary heating given had no significant effect on the friction. It is evident that, in the temperature range investigated, the important variable is not temperature, thus confirming the previous observations.

DISCUSSION

Using thick molybdenum disulphide films, unbonded by resin or other means, it has been found that the frictional characteristics of these films depend on temperature, rubbing time, and humidity, in such a way that only one explanation appears to fit all the observations. The conclusion reached is that the frictional resistance of molybdenum disulphide films to rubbing is not affected by temperature, as such, in the range of 20°–76° C; it is, however, strongly dependent on the moisture content of the film; μ decreases with increasing dryness of the film.

It is interesting to note that, where the present results are directly comparable with those of Johnson *et al*, very good agreement exists. However, their theory [7, page 7] that the decrease of μ with increase of temperature, observed with unbonded molybdenum disulphide at room humidity, arises from a decrease in intermetallic contacts definitely does not apply to the present results on thick molybdenum disulphide films, and indeed it is not the only possible explanation of their results. In fact, it seems not unreasonable to suppose that the present suggestion whereby the frictional characteristics are explained in terms of the dryness of the film applies equally well to Peterson and Johnson's results,[9,10] for it does offer an adequate explanation of all the important features of their results on unbonded molybdenum disulphide, namely:

(*a*) they observed a decrease of μ with increase in temperature, but this was only appreciable up to about 100° C, at room humidity;

(*b*) the frictional resistance, at constant temperature, increased with increase in ambient humidity (up to 70 per cent R.H.), and this was found even for very thick films for which, as they state, intermetallic contact was most unlikely;

(*c*) they found that the frictional resistance was lowest when the ambient humidity was <6 per cent and μ was then practically independent of temperature.

Peterson and Johnson make the following remarks about this last result, "At low humidity, there was very little change in friction with increasing temperatures; this would indicate that reduction in shear strength is insufficient to account for the reduction in friction obtained with increasing temperatures in room atmosphere."

On the contrary, what their results do show is that the shear strength is related to the dryness which can be controlled either by temperature or humidity, or a combination of these factors. If the humidity is low enough to dry out the film, then very little change of μ with temperature would be expected. If, on the other hand, the humidity is high, then there should be a marked dependence of μ on temperature up to about 100° C, as was indeed observed.

In addition, the above suggestion, now put forward, could account for the hitherto unexplained observation by Johnson, Godfrey, and Bisson [7] of a progressive decrease in μ with increase in sliding velocity; because increased velocity must have resulted in an increase in the temperature of the slider, and hence enhanced dryness of the molybdenum disulphide. But it may be unwise to compare the present results too closely with these latter results, as they were obtained from molybdenum disulphide bonded to steel by burning on it a molybdenum disulphide–corn syrup mixture, and the resulting film must have had a very complex composition. This comment also applies when considering the results of Bowden [2] and Barwell and Milne.[1] In these latter investigations, the interpretation of the results in terms of the lubricity of molybdenum disulphide is complicated by the presence of the sintered metal and metallic oxide (Bowden), and the resin bonding or the phosphate film (Barwell and Milne). The writer's recent results [8] do, however, show that, in the case of the phosphated steel, the phosphate crystals are brittle, very friable, soon removed from the bearing surface, and hence are unlikely to play an important part in the lubrication. Barwell and Milne's reported decrease of μ with increase in load, for two plane phosphated surfaces lubricated with molybdenum disulphide, may therefore well be a property of molybdenum disulphide itself, and could naturally arise from an increased molybdenum disulphide film dryness due to the greater frictional heating at the higher loads. The apparent contradiction between Barwell and Milne's results and those of Johnson, Godfrey, and Bisson,[7] who found an increase of μ with load, no doubt arises from the difference in geometrical shape of the test pieces used. In the latter case, a hemispherical-ended slider was used, and this is likely to have resulted in an increase in shear area with load—a factor which was later shown by Peterson and Johnson [9] to give rise to an increase in frictional resistance.

COMPARISON BETWEEN MOLYBDENUM DISULPHIDE AND GRAPHITE

The conclusion reached, that the frictional resistance of molybdenum disulphide films is greatly affected by the moisture content, μ decreasing with decrease in moisture content, is of considerable theoretical, as well as practical, interest, particularly when it is remembered that the friction of graphite is also moisture dependent (Savage [11]) but in the opposite sense to that of molybdenum disulphide, *i.e.* the friction of graphite increases with dryness. The reason for the moisture effect, and the difference in this respect between molybdenum disulphide and graphite poses a most interesting but difficult problem which it would be premature to discuss on the basis

of the evidence now available, but which offers an attractive field for further study.

One interesting and important practical point which follows from the above results is that a relatively high starting frictional resistance is to be expected if molybdenum disulphide lubricated sliding parts are left stationary for a sufficient time for moisture to be absorbed by the molybdenum disulphide. The rate of adsorption will obviously depend on the accessibility of the rubbing surface to the moisture, and to the relative humidity of the atmosphere, but, as a rough guide, the experimental evidence suggests that, at 20° C, and a relative humidity of 60 per cent, the most inaccessible parts between two bearing surfaces would be affected within a matter of hours, *e.g.* overnight. This suggests that the presence of an oil, or other hydrophobic liquid, may be desirable, quite apart from its lubricity, to reduce the moisture uptake of the molybdenum disulphide.

CONCLUSIONS

From the present results and those of other authors, it is considered that the observed dependence of the frictional characteristics of molybdenum disulphide on temperature and humidity arises from the fact that the frictional resistance of molybdenum disulphide films decreases with increase dryness of the film. It is concluded that this hypothesis is well supported by all the available evidence from the present and other authors' work and that the suggestion by Peterson and Johnson,[10] that intermetallic contact is an important factor in determining the frictional characteristics of molybdenum disulphide was certainly not applicable in the present investigation made on thick unbonded molybdenum disulphide films, and it is at least questionable whether their theory is justified on the basis of their own results.

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DISCUSSION

I. M. Wales: What degree of purity was the molybdenum disulphide? Savage has shown that very small amounts of organic material can alter the properties of lubricants very considerably. Is it possible that small traces of the ethyl alcohol used could have influenced the results?

I would also like to draw attention to a paper by Ballou and Ross.* The results obtained by these workers seem to be at variance with Mr Midgley's results. They went to very great length to obtain molybdenum disulphide as pure as possible. Particular difficulty was experienced in removing the oxide and the last traces of water.

J. F. Goodman and R. F. Deacon: We have been studying the variation in μ with temperature of MoS_2 films deposited from a suspension in water on platinum. Platinum was used to avoid any complications caused by metal oxidation. From the results of our experiments we should like to question the author on four points.

(1) In contrast with the author's results, we find that μ decreases with temperature up to *ca* 420° C, when a fairly rapid increase sets in, due to oxidation of the MoS_2 to MoO_3. The time of heating was very much less than in Mr Midgley's experiment (*ca* 10 min). Could this be due to a slow desorption of water, indicating that some has penetrated the lattice?

(2) It is thought that the thickness of the MoS_2 film has an effect on the μ-T curve. Did the author find any dependence of this kind?

(3) It was found that the MoS_2 powder could be very easily removed by milling, leaving a thin oriented layer of MoS_2. During the friction run it is suspected that metal to metal contact occurs. Has the author any definite evidence, *e.g.* by radio-active tracer technique or possibly electric diffraction photographs, that metal to metal contact does not occur?

(4) The author has shown that the final friction value is less than the initial one, even when moist air is introduced. Could this be ascribed to orientation of the MoS_2 during the experiment?

D. Summers-Smith: The two properties that appear to be essential for a solid lubricant to provide low friction are (1) a low shear strength in at least one crystallographic direction, and (2) a strong capacity for adsorption on the rubbing surfaces. These requirements are met by materials with a layer lattice structure. In crystals with this type of lattice the bond strengths between layers are much weaker than within the layers, and thus one of the postulated conditions is fulfilled. Again this layer crystallographic structure gives rise to plate-like crystals, which, by virtue of their form, tend to lie flat and may thus become strongly attached by van der Waals or weak chemical forces acting over a

* Ballou, E. V., and Ross, S. *J. Phys. Chem.*, 1953, **57**, 653.

large area. Both graphite and molybdenum disulphide have a suitable crystallographic structure, and yet they behave differently as solid lubricants, graphite being more effective in the presence of water vapour, while the reverse is true for molybdenum disulphide. The following hypothesis is given to account for this difference. These layer lattice crystals have the property of interstitially absorbing foreign atoms between the layers. Graphite, however, is a relatively inert material, and these interstitial atoms are held only by weak physical or, at the most, weak chemisorption forces. All surfaces under normal atmospheric conditions have absorbed monolayers of oxygen and water, and the interstitial adsorption by graphite will provide a mechanism whereby these surface layers can be removed from the metal to allow greater adsorption between it and the graphite. This effect will, no doubt, be accentuated by the increase in surface area produced by rubbing the graphite and also by the temperature rise produced on rubbing. Molybdenum disulphide, on the other hand, is a more active material chemically, and its layer structure occurs over a range of composition embracing the stoichiometric composition, giving rise to defect lattices. Interstitially adsorbed atoms may thus become, to a certain extent, bound chemically and, instead of reducing the shear strengths between layers, actually increase it, virtually by destroying the layer lattice. Thus, in the presence of water vapour, the lubricating properties of graphite are increased while those of molybdenum disulphide are reduced. The high coefficients of friction obtained with graphite in a high vacuum support the view that the shear strengths between the hexagonal layers are only sufficiently low to give low friction when interstitially adsorbed atoms are present. On the present hypothesis, it would be expected that molybdenum disulphide would still give a low coefficient of friction in a high vacuum. The boundary lubricating properties of water for plastics may be the result of a similar mechanism to that operating with graphite. The divergent results obtained with molybdenum disulphide by different investigators may result from the occurrence of the molybdenum disulphide lattice over a range of composition. It may be that optimum lubricating properties are possessed by crystals of the stoichiometric composition. Defect lattices would probably react more readily with oxygen, giving rise, as already postulated, to increased shear strength between the layers. Interstitial adsorption by graphite gives rise to an increase in the *c* axis of the hexagonal crystal, whereas chemical adsorption, as suggested for molybdenum disulphide, should result in change of this lattice structure. It should thus be possible to follow these changes by electron diffraction. It is suggested that future studies of the frictional behaviour of solid lubricants should be supplemented by electron diffraction studies.

In a number of graphs shown during the presentation of the paper, the author appears to attach significance to differences of 0·01 to 0·02 in a coefficient of friction of the order of 0·05. The coefficient of friction for any system is not a unique value, but, according to Bowden's theory, depends statistically on the formation, growth, and shearing of a large number of small contacts. Although, of course, it is possible to measure instantaneous coefficients of friction to 0·01 or less, it is common experience that, during any one experiment, variations of this magnitude and greater occur, and the repeatability between experiments is normally also of this order. I should be interested to have the author's comments on this point, and would like to know the repeatability of separate experiments in his investigation.

J. W. Midgley: I would like to thank I. M. Wales for drawing my attention to the work of Ballou and Ross. Their results on the adsorption characteristics of MoS_2 for benzene and water show a close parallel to the friction characteristics which I have found and lead to some very interesting conclusions. They have shown that the adsorptive capacity of MoS_2 for water vapour is due to the chemisorbed oxygen which is inevitably present on MoS_2 in contact with the air; MoS_2 itself is hydrophobic. In addition, Ross and Sussman * have recently shown that oxidation of MoS_2 proceeds at a significant rate even at temperatures as low as 85° C. Such a comparatively low temperature will readily be exceeded at sites of shear even under low loads. Since none of the frictional studies so far reported have been made on MoS_2 prepared and studied in an oxygen-free atmosphere, it is evident that a study of the frictional characteristics of pure MoS_2 has yet to be made. The results obtained from such experiments would be of distinct fundamental interest but probably of little practical value. The limits of impurities in the MoS_2 used in the present experiments were covered by the M.O.S. specification CS 2819 (5.8.1955) which are as follows: Silica $< 0{\cdot}02$ per cent, iron $< 0{\cdot}1$ per cent, copper $< 0{\cdot}05$ per cent, volatile matter $< 0{\cdot}10$ per cent, ether extract $< 0{\cdot}20$ per cent, $MoS_2 < 97{\cdot}5$ per cent, *i.e.* the powder contained a maximum of 2·5 per cent MoO_3. I cannot agree that the friction results which I have obtained are in any way at variance with the adsorption experiments of Ballou and Ross. On the contrary, the results of both investigations show the reversible nature of the adsorption of water vapour by MoS_2 in its normal oxidized condition. It follows that the effect on the friction of adsorbed water vapour is associated with the oxide layer which is always present on MoS_2 in contact with air. The hitherto unrelated friction characteristics reported by a number of different authors which have been confirmed and correlated in the present investigation are evidently due to this oxide layer.

The observed decrease of friction with rubbing time, as shown in Fig 3, is readily explicable as being due to the progressive decrease in film shear strength as the crystallographic orientation improves with rubbing. This might be termed the classical picture of the action of a solid layer lattice lubricant (*cf* Finch, Quarrell, and Wilman*). There is little doubt that this mechanism almost certainly contributes an important part to the observed lubrication properties of MoS_2; but it is now clear that this is by no means the whole story. The effects of humidity show that adsorbed water vapour also plays a significant role in the friction characteristics. Frictional heating will have a similar effect, reducing the amount of adsorbed water vapour, and hence must also, at least in part, be responsible for the observed decrease of friction with rubbing time. On the other hand, the subsidiary heating which was applied produced no detectable reduction of the friction (Fig 3). This apparent contradiction is readily understandable when the distribution of heat energy in the two cases is considered. Frictional heat is generated at the sites of shear, where its localized concentration will immediately result in desorption of water vapour. This occurs at the places where it will have the greatest effect on the friction, and hot spots generated will be at a temperature considerably above that measured by the thermocouple embedded in the backing. The subsidiary heating, on the other hand, was supplied via the mild steel backing and, being uniformly distributed, had a comparatively negligible effect on the friction.

The possible effects of adsorbed material on the friction of MoS_2, similar to those found by Savage with graphite, would certainly appear to be a very interesting field of study. Bearing in mind the good agreement between the present experiments and those of other workers who used a number of different methods of

* Ross, S., and Sussman, A. *J. Phys. Chem.*, 1955, **59**, 889.

applying the MoS_2, the ethyl alcohol used to disperse the power cannot have significantly affected the results reported here.

In my experiments the MoS_2 was heated only to 76° C, and no predictions have been made as to the effect of heating to higher temperatures. It is not evident, therefore, why my results can be said to be at variance with those of Goodman and Deacon. Their results do, however, appear to conflict with those of Peterson and Johnson, who found that the decrease of μ with temperature was only appreciable up to a temperature of 100° C, at room humidity. This apparent contradiction may well be due to the shorter time of heating in Goodman and Deacon's experiments. This could possibly be due to the desorption of water which had penetrated the lattice, presumably between the sulphur sheets, or if the observations were made on MoS_2 in a compacted film, it seems possible that the moisture adsorbed on the surface of the platelets could take ten minutes to diffuse out from the centre of the film.

It is difficult to comment more fully on the results quoted by Goodman and Deacon without a knowledge of the actual values of μ which they have obtained, and the conditions under which the observations were made. With regard to their observations of a dependence of the μ–T curve on thickness of the MoS_2 film, it is observed that the initial and final μ are repeatable, and for thick films they do not appear to depend on the film thickness. As stated in my paper, the time taken to reach the final value of μ varied considerably ($\frac{1}{2}$–3 hr). In this sense variations have been found in the μ–T curve, and this could be due to different rates of desorption of moisture from films of different thickness.

If thin films of MoS_2 are used, intermetallic contact is quite likely to occur, especially when the MoS_2 film has a lot of adsorbed water, since under these conditions the adherence of MoS_2 to the backing is poor. It was this observation that led Peterson and Johnson to the conclusions quoted in the paper, namely, that the decrease in μ with increase in temperature, observed at room humidity, is a function of decreased metallic contact resulting from the better adhesion of the MoS_2 to the substrate at higher temperatures.

As stated in the paper, the experiments on thick films were designed to eliminate the possible effects of intermetallic contact. At the end of each experiment the MoS_2 film thickness was measured and was found not to be less than about 0·2 mm, one hundred times the height of the deepest grooves on the backing annulus. Therefore, although similar results to those of Peterson and Johnson were obtained, their conclusions relating the temperature effect to intermetallic contact could not apply to the present results, and conversely, it follows that intermetallic contact cannot significantly have influenced their results. When studying the frictional characteristics of thin MoS_2 films, intermetallic contact is obviously a factor which must be carefully watched, but the results obtained show that there is no evidence to suggest that such an effect has yet been observed.

In reference to the comments made on the changes which occur in the MoS_2 film during sliding; it has only recently been realized that low shear strength in one crystallographic plane is not in itself a sufficient criterion for a good lubricant. If this were sufficient, then layer lattice materials would in general be expected to be good lubricants, whereas in practice this is not found to be true. Mica, which has a very well defined cleavage plane of relatively low shear strength, should on this score be a good lubricant when, in fact, it is not. As a result of an investigation covering a wide range of possible solid lubricants Peterson and Johnson have reached the important conclusion that good adhesion to the backing surface is also required. Considering the particular case of MoS_2, this conclusion seems to fit the observed behaviour very well, for the adhesion of MoS_2 for steel does appear to be better under drier conditions. One supposes that the effect of good adhesion of the lubricant to the backing is to promote the formation of an orientated layer with cleavage plane parallel to the surface, aided by the plate-like form of the crystals. It seems probable that the adhesion of the MoS_2 platelets to the backing is controlled by the oxide, which must cover the external surface of the MoS_2 exposed to atmospheric air. As Ballou and Ross have shown, the adsorptive capacity of MoS_2 for water vapour arises from the presence of oxide. When moisture and oxygen are freely available there will be little encouragement for the platelets to adhere to the backing. Under drier conditions, however, the adsorbed water on the backing perhaps offers a strong attraction to the platelets, resulting in the stronger adhesion which is observed under these conditions.

As regards the changes which occur during sliding, with particular reference to the results shown in Fig 2, my opinion is that as rubbing proceeds the orientation improves, and that this is facilitated by the improvement in adhesion of the MoS_2 to the backing which occurs under the drier conditions. As the orientation improves so the friction decreases. If, after this, the bearing is allowed to cool in dry air, or, presumably, in vacuum, then the adhesion of the MoS_2 to the backing will remain good and the friction low; but if the bearing is cooled in moist air, then the adhesion of the MoS_2 to the backing decreases, the MoS_2 film becomes partially disorientated, and the friction increases, although not quite to its original high value, owing to the persistence of some of the previously acquired orientation.

Dr Summers-Smith's careful analysis contains a number of very interesting points. His hypothesis regarding the behaviour of graphite is attractive, but I am far from convinced by that relating to MoS_2. On his view the dependence of μ on moisture for MoS_2 arises from chemisorption destroying the layer lattice. The feature which most clearly distinguishes chemisorption from physical adsorption, however, is the irreversibility of the former. It is true that if the specimens were not disturbed, other than by starting and stopping, an irreversible decrease was found after the first run, as shown in Fig 2. Subsequent runs, however, showed that if the specimens were not disturbed between the runs there was no further irreversible decrease in μ, and if the surfaces were parted between each of a series of runs on the same specimens, on restarting the friction reverted to its initial high value of $\mu = 0{\cdot}2$, at room humidity. These results led to the conclusion that the determining process taking place in the present experiments, and those of other authors quoted in the paper, is one of physical adsorption, not chemical. Chemisorption will also be taking place, since MoS_2 is quite a reactive material; ball milling in atmospheric air, for example, is sufficient to cause substantial oxidation, and this is a closely allied process to that being studied here. From the reversibility of the process it is clear, however, that the amount of oxidation which occurred during the experiments was insufficient to affect the results.

In regard to the repeatability of experiments: ten separate series of runs were carried out using a number of different loadings, temperatures, and humidity sequences. Four independent values of the initial friction were obtained, they were all in the range $\mu = 0{\cdot}18$–$0{\cdot}19$. The nine independent values of the final μ obtained all fell in the range $\mu = 0{\cdot}055$–$0{\cdot}057$. The system was deliberately heavily damped, the stick–slip fluctuation being only ± 3 to ± 5 per cent. It should be made clear that these results were all obtained on one batch of Murex purified natural MoS_2 powder, but the close agreement between the results and the published work of others on natural MoS_2 powder, especially as to the effects of humidity, temperature, and rubbing time, amply confirm their more general validity. Under the circumstances there-

fore it was thought justified to quote the results to two and, where possible, three significant figures. The form of the specimens, two annuli, the uniform distribution of load over them, and the reduction of stick-slip to a minimum all contributed to the reproducibility obtained; for the real speed, load distribution, and frictional heating were reasonably constant, controllable, and measurable.

It was found that the effects of humidity, temperature, and rubbing time on the frictional characteristics of a synthetic MoS_2 powder were very similar to those reported on the natural MoS_2 powder, and the final friction, $\mu = 0{\cdot}055$, was the same within the experimental error. The initial friction was, however, significantly higher, being $\mu \simeq 0{\cdot}4$. Whether this was due to the moisture content of the synthetic material being initially about three times greater, or to its smaller crystal size, is not yet certain.

SOLID LUBRICANTS*

By E. A. SMITH†

INTRODUCTION

IT is doubtful whether one can classify a solid lubricant as a good one, of medium quality, or of poor quality. One can, perhaps, say that a particular solid lubricant is more versatile than another, or that it performs much better in a particular use than another. It is important to relate the criterion of such a lubricant to the particular use, but one cannot generalize. For example, one knows that graphite will lubricate effectively the dies used in the drawing of filament wires, whereas talc is ineffective. There will be occasions where the ceramic qualities of talc may make it more suitable than graphite. Further, molybdenum disulphide may offer advantages over graphite for certain classes of work, the position being reversed in other classes.

What is the real function of a solid lubricant? Essentially it is to keep two rubbing faces apart, which would otherwise score each other or weld together. If one accepts this broad concept one can admit numerous substances to the family of solid lubricants. Of the many in existence, however, there are comparatively few which are of real practical value, for one reason or another, while economic or technical reasons may militate against some which appear promising.

A liquid lubricant functions as such by interposing layers of molecules between two rubbing faces, the shear strength between the layers being small. The action of a boundary film is essentially one of parting, in that the adhesion forces between the rubbing faces are satisfied by the oil molecules. A solid lubricant not only satisfies those adhesion forces but also introduces, like the fluid oil film, a layer in which the shear forces are weak. One might say that the difference between a solid lubricant and a liquid substance is largely a matter of degree. It is interesting and significant to observe that graphite yields a coefficient of friction of between 0·05 and 0·15 which is the same order as the values obtained with a boundary film of oil.

STRUCTURE ASPECTS

It is evident that structure is the principal factor in determining whether a solid has bulk lubricating qualities. How effective is the solid depends on its degree of weakness in shear. R. H. Savage has maintained that graphite lubricates because of its adsorptive properties, but clearly that unusual adsorptive property springs from the fact that graphite can shear easily, with basal cleavage and so expose virgin faces. Thus, structure is the primary cause for lubrication and absorption a secondary one, even though the latter may be important. Diamond offers a low coefficient of friction when sliding occurs on a crystal face, but it is not a bulk lubricant, the structure requirements mentioned not being fulfilled. Polytetrafluorethylene, boron nitride, cadmium iodide, tungsten sulphide, and other solids offer a structural feature in one way or another which qualify them as bulk lubricants. Similarly, molybdenum disulphide and certain cleavable minerals.

When the structure permits cleavage one has to satisfy oneself that the hardness and other physical characteristics of the platelets that result from cleavage are satisfactory. Here one finds certain substances, like mica, beginning to depart from ideal requirements. If one could ensure perfect basal orientation of the mica platelets between two rubbing faces the resulting separation of the metal would lead to minimum wear, but if the mica turns end on to the surfaces its high mechanical strength across the basal plane would lead to a condition resembling that of any non-cleavable material. There are other factors also which militate against mica, as, for example, its tendency to aggregate strongly when reduced to a fine powder. There is also the loss of the perfect laminar structure when one grinds mica, the material tending towards the amorphous condition. From these brief remarks it will be seen that there are ancillary requirements in a solid lubricant to be met, in addition to structure.

GRAPHITE IN LUBRICATION

Graphite has taken the leading position among the solid lubricants because it fulfils most of the requirements mentioned above. It has a laminar structure, it is chemically inert for all practical purposes, and when it is size-reduced by rubbing it maintains its laminar form. The regularity of the atom spacing in graphite is illustrated by the transmission electron diffraction pattern in Fig 1 obtained by H. Wilman.

* MS received 3 February 1956.

† Acheson Colloids Ltd.

The structural behaviour of graphite during rubbing makes an interesting study, which one can trace with X-ray diffraction. If one takes a sieve-size powder the resulting structure can be expressed by the X-ray photometer analysis of Fig 2 (*a*) which indicates that the carbon sheets are extensive and regular. When the powder is rubbed down until the majority of particles have a diameter around 1 μ there is a modification of the structure shown in Fig 2 (*b*). What this means in terms of structure is indicated schematically in Figs 3 (*a*) and (*b*), from which it will be seen that the carbon sheets have been reduced in area and there is a

Fig 1

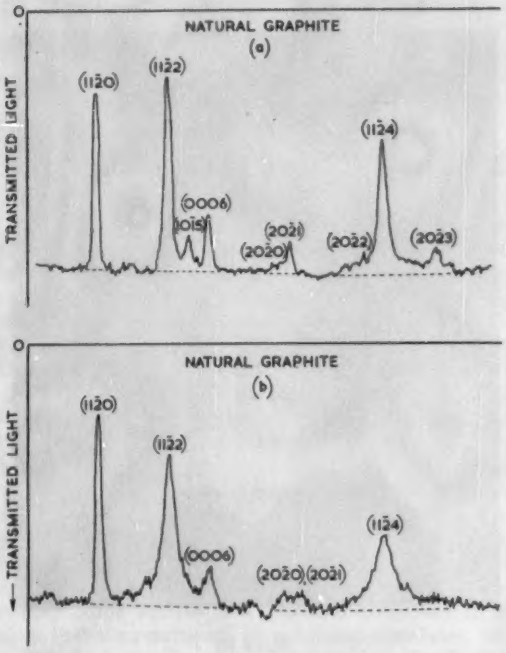

Fig 2

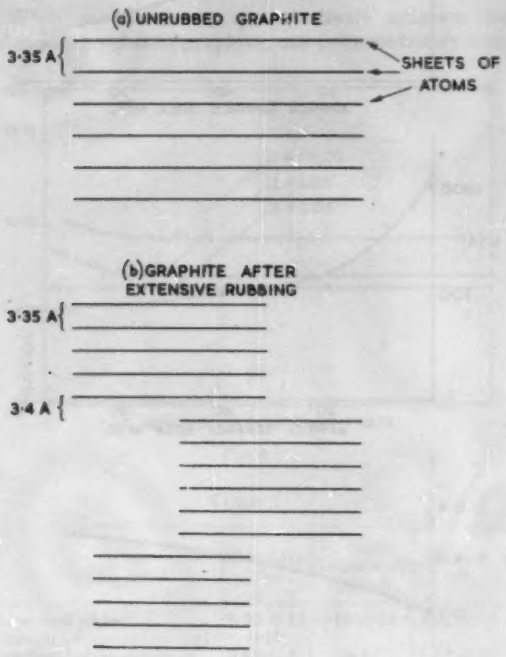

Fig 3

tendency for the sheets to be repeated in an $ABC \ldots ABC$ sequence instead of the $AB \ldots AB$ sequence. This change is shown quantitatively in Fig 4.

To see whether these structural changes in graphite with an increasing amount of the rhombohedral modification of the hexagonal lattice has any practical significance, an examination of the friction and adsorptive capacity of graphites of increasingly finer particle size was made. No differences of friction values have been noted which could not be accounted for by experimental errors and other defined factors. It would appear, however, that the graphite tends to become more surface active as the particle size is reduced, but here again, the practical significance in lubrication is not yet clear.

In case it is thought that the structure changes picked up with X-ray diffraction are unique for graphite it should be added that changes have been noted in molybdenum disulphide and in such cleavable minerals like biotite and vermiculite. These latter two minerals show pronounced cationic exchange

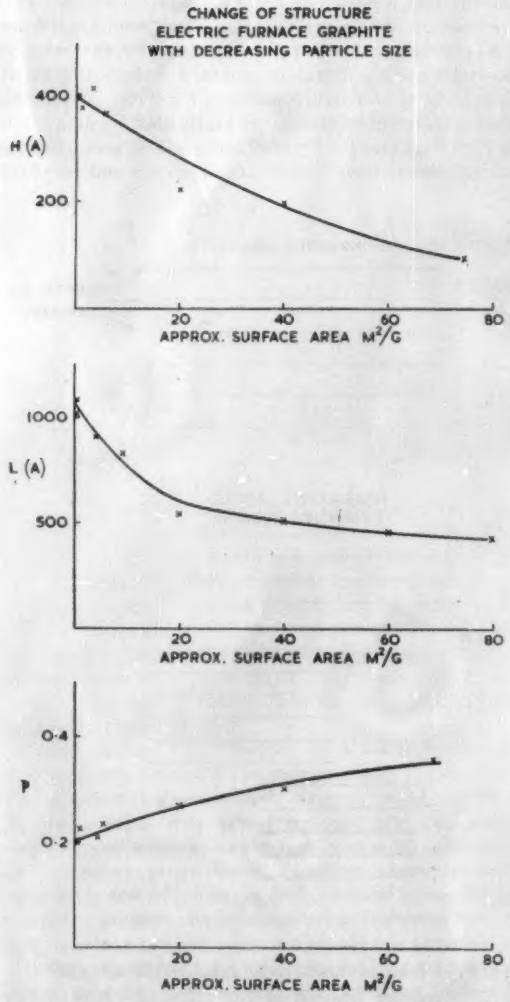

FIG 4

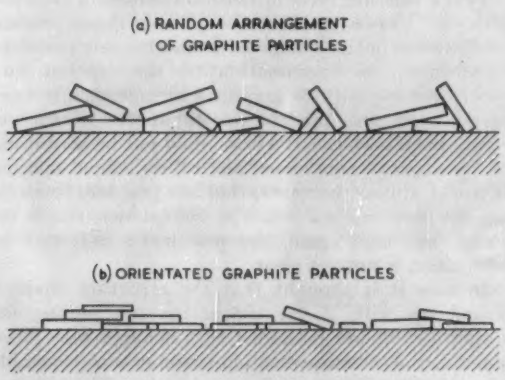

FIG 5

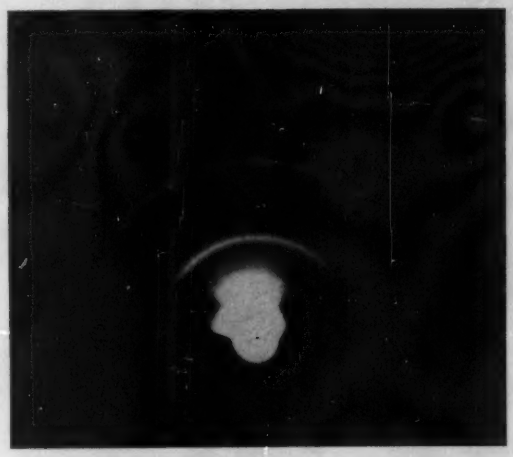

FIG 6 (*a*)

FIG 6 (*b*)

properties with size reduction, becoming more active, which fits in with the observations on graphite.

ADSORPTION OF GRAPHITE TO METALS

It was Mabery [1] who first showed that graphite appeared to become adsorbed to metal when used in lubrication of the metal. Since then Matthews and Wolf [2] measured quantitatively the amount of graphite adsorbed to a bearing. Jenkins [3] and then Finch [4] established optically the existence of what is now known as an adsorbed graphoid surface on metals rubbed with graphite. If one puts graphite particles on a metal surface a characteristic disorientation is obtained, as indicated by Fig 5 (*a*), which on rubbing,

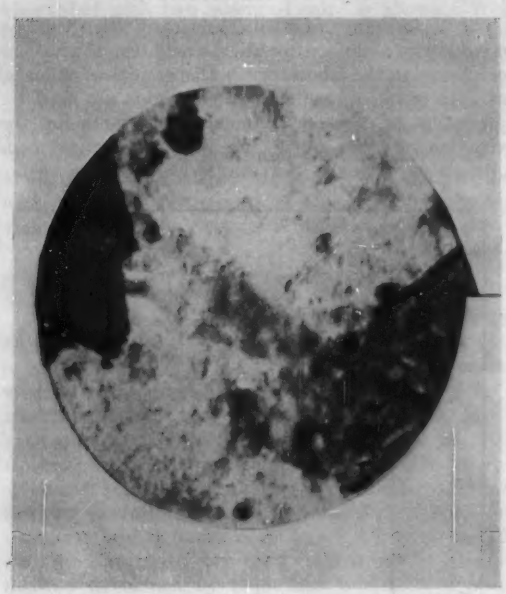

Fig 7

gives an orientation as in Fig 5 (*b*). It is a fact that the lightest rubbing produces orientation of the graphite particles, this condition being, of course, necessary for maximum lubrication. Figs 6 (*a*) and (*b*) are the electron diffraction patterns for the conditions shown in Figs 5 (*a*) and (*b*).

It has been known for some time that one can rub particles of graphite down to a matter of a few mμ thick. They become translucent, and are optically pleochroic with a refractive index of 1·95. The substance continues to be slippery at this extreme thinness, for one is still dealing with many layers of carbon sheets in the lattice, with their characteristic weakness in shear. It is difficult to locate very thin platelets on the rubbing surface of bearings, but more recently some success has attended this, and it is hoped that the results will be published elsewhere. A typical electron micrograph is shown in Fig 7, the upper dark area being part of a graphite platelet and the lower area indicating a very thin platelet with the metal substrate still visible. A more detailed examination is also in hand, in England, of the effect of particle size, oil carrier, rubbing pressures, and other factors in the formation of an adsorbed graphoid layer on rubbed metal.

FRICTION VALUES OF GRAPHITE

When one decides to quantitatively estimate the lubricating value of graphite, one is immediately con-

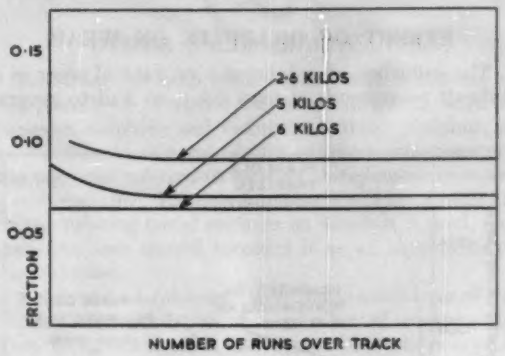

Fig 8

Table I

	Graphite film	Unlubricated metal	Mineral oil
Three-ball slider . .	0·09–0·12	0·16–0·18 *	0·15–0·17
Plane slider (reciprocating)	0·15	—	—
Bowden–Leben machine .	0·07–0·1	0·4	0·17–0·22
Modified Deeley instrument	0·12	0·6	0·15
Rollers	0·05	—	0·07

* Surfaces washed with oil solvent but not chemically clean.

Table II

Machine	Description	μ Graphited oil	μ Mineral oil
Deeley	Plane horizontal disk rubbing against three flat-edged studs arranged in a circle on an upper disk which is free to rotate parallel to the lower disk. Rubbing speed 20 f.p.m., pressure 50 p.s.i.	0·04	0·05–0·06
Thoma	Two steel cylinders running against one another on inclined axes, one at 50 rev/min and the other at 300 rev/min. Sinusoidal line contact; load (estimated) 42,000–125,000 p.s.i.	0·075 0·042	0·077 0·045
Bowden–Leben	Cylindrical member resting on a plane surface which is drawn along by hydraulic ram.	0·06	0·08–0·12 *
Cold rolls in sheet-metal working	Polished steel rolls 6 inch dia 20–30 rev/min sheet reduction 22%.	0·068	0·082
Journal bearing	Steel journal in white-metal bearing 2 inch dia, 500 rev/min. Loads 500–2000 p.s.i., 80° C.	0·001	0·001

* Compounded oil.

fronted with a mass of data, some of which, at first sight, presents anomalies. The actual friction value yielded by graphite would depend on the testing, machine and the conditions of testing. Thus, laboratory machines yield values which lie around 0·1, while under loads which cause metal deforming, as for example, strip rolling and wire drawing, the values appear to be around 0·06–0·08. Some values for dry graphite without and with oil obtained on various laboratory testing machines are shown in Tables I and II. Fig 8 provides an indication of the uniformity of graphite lubrication in terms of friction.

EFFECT OF GRAPHITE ON WEAR

The influence of a lubricant on rate of wear is a difficult assessment, at least for it to lead to general

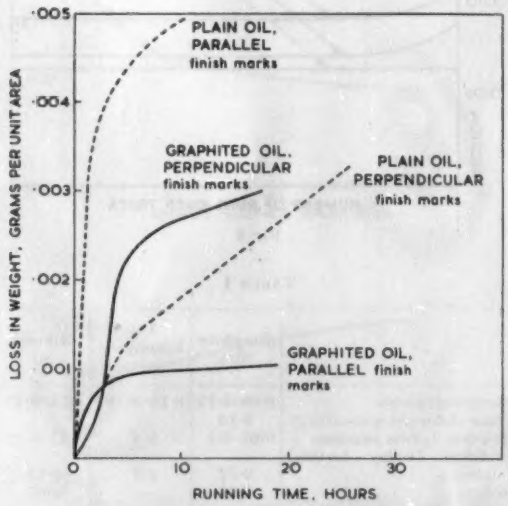

Fig 9

conclusions. For that reason the data on this are confined to an interesting series of results obtained under controlled laboratory testing. It shows how the slippery platelets of graphite modify the character of wear by lying between opposite rubbing faces. Two surfaces carrying finish marks parallel to each other were rubbed and the rate of wear measured. Such a condition is difficult for adequate oil lubrication, and the rate of wear is high initially. When the surfaces are run with finish marks perpendicular to each other the rate of wear is lower, because the " ridges " saw upon one another, with minimum area of contact. When graphited oil is substituted for the plain oil the rate of wear is appreciably reduced in one instance and initially modified in the other. These effects are shown quantitatively in Fig 9.

On a practical scale it is known that finely divided graphite of requisite purity in oil, known as collodial graphite, will reduce initial wear in rubbing faces, and is consequently used widely as an additive to help the lubrication of mechanical equipment under the severe conditions of running-in.

The ability of the graphited surface on rubbing faces to offset metal pick-up and seizure will lead to a lower rate of wear. It is necessary, incidentally, for a slippery film of graphite to have formed on rubbing faces to obtain the maximum effects of this solid lubricant. In a four-ball testing machine, where the duration of the test is quite insufficient for a graphoid layer to form, one would expect no positive results when colloidal graphite is added to oil. This time factor cannot be emphasized too strongly if one is to draw correct conclusions from mechanical tests.

INDUSTRIAL ASPECTS

The performance of a solid lubricant when used on an industrial scale is, after all, the acid test of what has been found in the laboratory. Dispersions of colloidal graphite in oil, water, and other liquids are used for lubrication of new mechanical equipment, for the extrusion of light alloys, where it has proved conspicuously successful, for non-ferrous wire drawing,

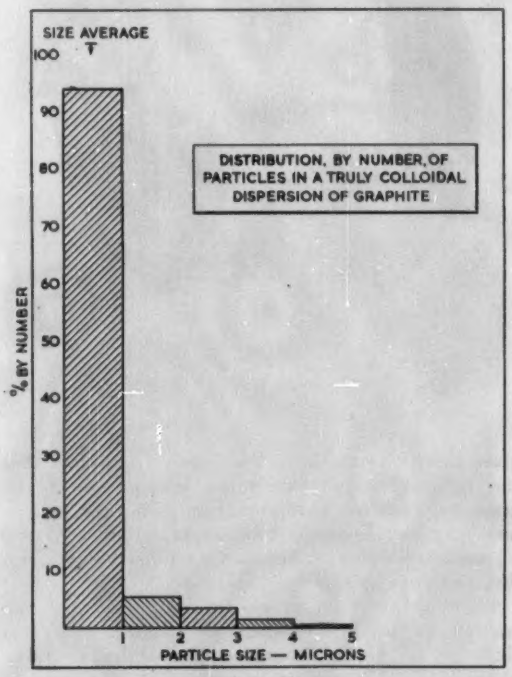

Fig 10

for die forging, dry and oil-less lubrication. It is not possible to do more than touch on the major uses of this useful additive.

A note on the practical use of graphite should, however, be added before closing one's remarks on this solid. For most industrial uses the graphite should be pure, around 99·8 per cent, and so finely

divided that it will remain suspended in oil and pass through conventional filters. This is achieved by colloidalizing the graphite, and a typical size-range achieved today is shown in Fig 10. When correctly stabilized such a diluted dispersion should remain suspended in, for example, an SAE 30 oil for months, with less than 5 per cent settling from the topmost layers, with no sediment. One could pass such a dispersion successively through more than twenty No. 1 Whatman filter papers, which conveys an idea of what one is dealing with.

MOLYBDENUM DISULPHIDE

The arrangement of the lattice of molybdenum disulphide gives layers of molybdenum atoms alternated with two layers of sulphur atoms. What has been said of graphite applies in a large measure to MoS_2, except that the latter begins to decompose below 400° C, and rapidly at that temperature, giving molybdenum trioxide as the principal by-product. The coefficient of friction tends to be a little lower than for graphite, while changes in structure are noted for MoS_2 on size reduction. It is not proposed to deal with the frictional aspects of this solid lubricant in view of J. Midgley's separate remarks on the subject.

GLASS

Attention has been focused in the past year or two on the possibilities of glass as a lubricant. The glass is melted on the workpiece and acts in much the same way as a liquid lubricant. By selecting glass of various melting points one can cover several alloys, each alloy having its characteristic softening point for working or forming. This technique is offering considerable promise in ferrous and non-ferrous tube forming operation, the forging of stainless steels and titanium, and is under consideration for use in light alloys. Except to say that glass is applied by the method developed by Sejournet, and also as a dispersion of finely divided glass in liquids, it is a little early to predict the best way of using this interesting approach to lubrication. It might be added that the spray coating of the billet with glass dispersions assists in reducing scale during heating before forming. One can say, however, at this stage that glass offers a promising avenue of high temperature lubrication in the metal industry.

TALC AND MICA

It has been pointed out by observers that talc and mica do not offer a low enough friction value to qualify as solid lubricants, but it should be added that there are conditions in industry where excessive heat and pressure set one's aim at merely parting two surfaces. If one can keep two rubbing faces from welding together one has achieved something. Therefore, talc and mica should not be ruled out, especially as they both have ceramic qualities and are chemically inert.

CAMPHOR

At the moment this interesting substance is more of academic interest, because its sublimation temperature is too low for use in the general run of lubrication. Its remarkably low coefficient of friction, comparable to PTFE (polytetrafluorethylene), suggests that there is still much to be learned about solid lubrication. It is possible that camphor gives rise to a gas cushion effect on volatilizing, for it can be shown that camphor reduces friction to a value comparable to oil under boundary conditions in an operation such as strip rolling.

OTHER SOLID LUBRICANTS

Reference has been made earlier to the existence of compounds of potential value as lubricants, such as tungsten sulphide and cadmium iodide. Sulphur, as an additive to mineral oils for extreme pressure work has not been referred to because this element occupies a mid position. Its main function is to form a sulphide on the rubbing metal surfaces on which it is used, and therefore, one should consider it as an intermediate, like chlorine.

Peterson and Johnson [5] have made a call-over of the friction characteristics of a number of compounds. They bring out the fact that some solids whose crystal structure would not encourage one to think of them as lubricating do, in fact, give low coefficients of friction, while those with a laminar form do not lubricate. The following are some of interest; SAE 60 mineral oil providing a coefficient of 0·10–0·13 under the testing conditions:

	μ, 1 minute sliding	μ, 30 minutes sliding
Cadmium iodide (CdI_2)	0·04	0·06
Cadmium chloride ($CdCl_2$)	0·03	0·07
Cobalt chloride ($CoCl_2$)	0·04	0·10
Copper bromide	0·04	0·06
Silver sulphate ($CuBr_2$)	0·14	0·14
Zinc stearate	0·07	0·11
Mercury iodide (HgI_2)	0·18	0·18
Silver iodide	0·19	0·25
Titanium disulphide	0·20	No lubrication
Boron nitride	—	—
Mica	Failed to lubricate	
Talc	Failed to lubricate	

If a solid fails to adhere to a metal face, like boron nitride or mica, it will not appear to offer any promise as a lubricant. As previously mentioned, whether it facilitates sliding to be considered as lubricating in the broadest sense depends on the practical conditions under consideration, and also on how one uses the solid, *i.e.* whether in a carrier medium and whether it is used in conjunction with a bonding agent. One would have to look carefully at certain chlorides which offer a low coefficient of friction but which are corrosive, as for example, mercuric chloride.

Sometimes interesting results can be achieved by combinations of solids, as for example, Teflon and molybdenum disulphide (1 : 1), which gives, according to Milz and Sargent Jr.[6] a coefficient of friction between 0·13 and 0·21. Teflon–asbestos (3 : 1) yields a value

of 0·14 to 0·21, and Teflon–copper (1 : 1) a value of 0·13 to 0·20. For comparison the coefficient of friction obtained with nylon was 0·15 to 0·33 and polystyrene, 0·12 to 0·45.

CONCLUSIONS

The subject of solid lubricants is an extensive one, and in the above notes it has only been possible to touch on salient features. One might say that the chapter is opening, for present knowledge of crystallography suggests that one may, before long, be able to tailor-make a structure in a solid to provide special features in much the same way as the oil technologist can now assemble his closed and open chain compounds for liquid lubrication.

ACKNOWLEDGMENTS

The author thanks Dr H. Wilman of Imperial College, London University, for the transmission electron diffraction pattern of graphite, and Dr G. E. Bacon of AERE, Harwell, for the plot of structure changes in graphite.

It is also appropriate to mention that 1956 happens to be the centenary of the birth of Dr Edward G. Acheson (1856–1931), who developed the first industrial method of making pure graphite in the electron furnace. He also gave to the world, in 1891, a thermal method of manufacture of silicon carbide, so providing industry with the softest and hardest of minerals.

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DISCUSSION

J. F. Goodman and R. F. Deacon : Is the " shearing " process envisaged as being a parallel movement of two neighbouring planes, or as a " peel " rather like the cleaving of mica? The stress necessary for the latter will be considerably less than for the former, and adsorbed vapours will also have a reducing effect. If it is a peeling mechanism, *i.e.* a tensile failure, does it affect the theories of structure as determining lubricating properties?

E. A. Smith : I do hold that there is a basal weakness in shear in graphite. It is not possible to say, however, what is the magnitude of the force required to displace one layer in the lattice with respect to the other, seeing that it cannot be said whether or not this weakness contributes directly to the lubricating effect of graphite, or whether the act of shearing uncovers virgin surfaces which readily adsorb impurities, along the lines indicated by R. H. Savage. That the weakness in shear plays a part in the lubricating effect is indicated by the work of Campbell, who found that oriented graphite platelets gave characteristically low friction values in vacuum.

A detailed consideration of the graphite lattice does not throw much practical light on the question of whether the material shears when rubbed or " peels." It is rather difficult to accept the suggestion of Goodman and Deacon, that cleavage of graphite might take place by the " peeling " action rather than by shear. It may be true that thermodynamic considerations point to simple shear of the lattice as being unlikely, but such a conclusion would be based on inadequate knowledge of the exact nature of the lattice with which we are concerned. There are still many unsolved problems regarding the structure of graphite. For example, the Phase Rule tends to discount the possibility of the existence of rhombohedral symmetry alongside a hexagonal symmetry in graphite, but the fact remains that the two have been observed in X-ray diffraction analysis. We seem to be confronted with a series of anomalies in the findings on graphite, which makes one reluctant to try to assert the nature of the changes in the graphite lattice when rubbed.

One possible objection to the suggestion that graphite platelets might " peel " off, rather than shear, is that such a tearing action would probably lead to a disturbance of the parallel carbon sheets in the vicinity. There appears to be no published evidence to reveal such a disturbance. On the other hand, the existence of a skew arrangement of the parallel layers has been amply demonstrated, the layers, however, remaining always parallel, but our state of knowledge of the subject makes it inadvisable for one to dogmatize on this matter.

There appears to be a difference in the mode of action of graphite and mica when rubbed, which suggests that the process of cleavage is different. Thus, if one rubs very lightly over a mica surface, the rubbing member should pick up no particles of mica, whereas if one rubs very lightly over a graphite crystal, it is very difficult, if not impossible, to avoid the removal of platelets from the surface of the graphite. The marking power of graphite on paper gives a simple demonstration of this action. If the " peeling " mechanism suggested by Goodman and Deacon can be proved, it would undoubtedly affect our thinking about the mechanics of graphite lubrication.

The above considerations concern the picture which is generally conceived, in which rubbed graphite spreads over a metal surface like a series of playing cards. This picture need not conflict with thermodynamic considerations of the lattice, if one thinks of the platelets or particles as packets of finer platelets. A macroscopic effect is dealt with, rather than a breakage of the lattice in graphite. The mere act of drawing a line on paper with pencil is no more than a spreading out of a series of graphite platelets which overlap one another on to the paper. If one rubs the graphite line, it can be worked out into a smudge which is the spreading of the packets of platelets to give greater coverage.

Whenever graphite is reduced to fine particles, the latter assume a platelike shape, and the ratio of length to depth of these platelets has been measured by various means and by various observers. The natural tendency for graphite to break down in this way to platelets does presuppose a weakness in shear, which brings us back to the original Bragg concept about the primary reason for the lubricating action of this material.

J. H. Harris : There seems to be a great deal of evidence accumulating on the behaviour of solid films of graphite

and MoS_2, including the latter bonded to the metal surface, but not very much experimental evidence on their behaviour dispersed in liquid or plastic solid (grease) lubricants.

A great deal of work remains to be done on the effect of variation of proportions and particle sizes of the two solid lubricants in such dispersion.

In this connexion, can the author communicate information on :

(1) The type of " plain oil " described in Fig 9 ?
(2) Whether it is the base oil used in the " graphited oil " ?
(3) What percentage of graphite, presumably of the type known as colloidal, was incorporated in the graphited oil ?

E. A. Smith : The following may supplement the data in the paper:

(1) The " plain oil " described in Fig 9 was a straight mineral oil (paraffinic) of SAE 10 viscosity.
(2) The identical oil was used to carry the colloidal graphite in the product described as " graphited oil."
(3) 0·2 per cent colloidal graphite by weight was incorporated in the graphited oil.

. It is agreed that there is much work to be done on the effect of variations of percentages and particle sizes of graphite and molybdenum disulphide. It might be added that while particle fineness is essential where a product is used in an engine or system involving oilways and filters, in coarse metal-forming operations a larger particle size can be desirable, and, in point of fact, is used.

B. E. Hurley : It would appear that a solid lubricant, to be effective, must be firmly attached to the metal surfaces involved. How can the various solid lubricants mentioned, including molybdenum disulphide, be made to adhere to the large contaminated surfaces, such as piston rings, cylinder bores, gear teeth, and journals, which are used in practical engineering ?

E. A. Smith : The pressure between the rubbing surfaces appears to be sufficient to rub graphite, for example, on to the metal. Once graphite and molybdenum disulphide are pressed into contact with the metal they tend to adhere, and in some instances may be incorporated into the flowed surface layers of metal, to give a low friction skin. Evidence obtained in the electron microscope is now available of the existence of adhering graphite to the cylinder walls of an engine lubricated with graphited oil, which, it is anticipated, will be published elsewhere.

D. Summers-Smith : The mention of boron nitride as a solid lubricant was very interesting. This material has enjoyed such a reputation for some time, though no evidence in the published literature has been found to support this. We have recently considered the possibility of using solid boron nitride as a ceramic material, and its frictional properties have been of some concern. Although the solid material has a distinctly slippery feel, it was a surprise to find that it did not give particularly low friction. The coefficients of friction between two boron nitride surfaces and between boron nitride and mild steel varied from 0·2 to 0·3 at 20° C, rising to 0·4 to 0·5 at 200° C.

B. I. Callin : In the table on p. 327 no values are quoted for the coefficient of friction of boron nitride. Have you any values at all for this material, either in your own work or other sources ?

At Thornton there has been occasion to examine a sample of boron nitride on the Bowden–Leben machine. The sample used gave an X-ray pattern which indicated that a large proportion of the material had a lamellar structure but was poorly crystallized.

Mellor's treatise states that boron nitride prepared at lower temperatures is readily soluble in aqueous ammonia, but that the high temperature type is not. The present material did not appear appreciably soluble. However, the following table includes friction data on a " saturated " solution in aqueous ammonia, although it is not known how much nitride, if any, had been taken into solution.

All the tests were carried out at a relative sliding speed of 0·005 cm/sec, using a load of 2 kg. The boron nitride was applied in three different ways :

(1) Dry powder rubbed into the plate.
(2) 10 per cent slurry in water applied as a thick film.
(3) " Saturated " solution in aqueous ammonia (see above).

The values obtained for the coefficient of friction at 20° and 120° C were as follows :

Method of application	Coefficient of friction	
	20° C	120° C
(1)	0·30	0·26
(2)	0·24	0·24
(3)	0·29 *	0·37

* Stick–slip motion. Maximum value quoted.

These figures indicate that the sample of boron nitride was not a good boundary lubricant compared with such materials as molybdenum disulphide, graphite, etc. The insolubility in aqueous ammonia and the X-ray data seem to suggest that the sample is probably of the " hot-fired " type, but there is no indication of any associated low friction values.

E. A. Smith : I have described the function of a solid lubricant as one of keeping two rubbing faces apart, which definition admits numerous substances to the family of solid lubricants. This definition does not rely upon the coefficient of friction as a criterion, and indeed, it can be misleading to rely upon friction values in, for example, metal-forming operations. Boron nitride merits consideration as a lubricant because of its bulk properties. That its friction is higher than graphite or molybdenum disulphide would not reveal the experimental fact that it gives a low wear value in oil, which is comparable to these solid lubricants. There is some uncertainty about the exact type of boron nitride required for best results, except that it must be " hot-fired."

The Bowden–Leben machine is a reliable guide to friction values, but one must be careful in using these as the sole criterion of an industrial lubricant or potential lubricant. For example, pure graphite can show a friction value of around 0·12, compared with, say, 0·15 for mineral oil, and yet the former is conspicuously successful in heavy industrial work, such as metal-forming, whereas the latter is, generally, useless for such work.

The elegant work of Dr Bowden and his associates, over the years, has brought out the need to look farther than friction for evaluation of a lubricant. In particular, one cannot relate friction to the wear resistance of a lubricant.

SOME LUBRICATION PROBLEMS OF AVIATION GAS TURBINES*

By V. W. DAVID,† J. R. HUGHES,† and D. REECE†

SUMMARY

A brief description is given of the lubrication requirements of aviation gas turbines. New data are presented which show that the load-carrying capacity of synthetic lubricants and, in general, oils containing EP additives decreases with increasing speed and, with the EP oils, may reach the base oil level at speeds corresponding to those found in practice. Low-temperature studies on mineral and synthetic oils on two current gas turbine engines in the cold room have shown that, in the case of mineral oils, the extrapolated and not the measured viscosity is the main factor influencing both the starting torque requirements and low-temperature oil pumpability in these engines. Thus, mineral oils, though showing some low temperature limitations for use in gas turbines, are not so bad as their pour points would suggest, and should give perfectly satisfactory performance in suitably designed engines where the minimum oil temperatures are not extreme.

LUBRICATION REQUIREMENTS OF AVIATION GAS TURBINES

THE application of the gas turbine engine during the second world war to aircraft propulsion has resulted in a revolution in aircraft development, since it has enabled engine power to be considerably increased, thrusts equivalent to about 19,000 h.p. being possible in the latest designs. The place of the gas turbine engine in military aircraft is now assured; in the civil field a gradual replacement of the piston engine is to be expected.

The lubrication requirements of gas turbine engines differ markedly from those of the piston engine. The bearings are invariably of the ball or roller type and are subjected to more or less constant loading compared with the cyclic loading experienced in the piston engine bearings. On the other hand, bearing temperatures, particularly those of the turbine bearings, are high—in the region of 200°–280° C at the present time, depending upon engine design. Since rotational speeds are much higher than those in the piston engine, the propeller reduction gears must be of higher ratio, and gear sliding speeds are necessarily higher. Gear loading is as high as possible, in the interests of keeping weight to a minimum.

As well as lubricating gears and bearings at very high operating temperatures, the lubricant must allow the engine to be started at the very low temperatures encountered on aerodromes in certain parts of the world. With piston engines fuel dilution provides a ready answer, but with the gas turbine engine this method is impracticable, since the fuel is less volatile. Hence, the lubricant must be fluid down to the lowest ambient temperatures encountered.

These requirements make exacting demands on the lubricant. The high temperatures call for lubricants of exceptional resistance to chemical degradation and oxidation. This problem is aggravated by the fact that in most engine designs the total oil capacity is less than 10 gal, and the oil consumption, and hence the rate of addition of new oil, is very small and the oil is expected to function satisfactorily for hundreds of hours between engine overhaul periods. In future, the problem of high temperatures is likely to become even worse as aircraft fly at speeds up to Mach 2·5. At such speeds the temperature of the air on entering the compressor may reach 250° C, whilst cooling by normal means becomes impossible because of high skin temperatures. Bulk oil temperatures are therefore likely to be well above 250° C, with consequent further likelihood of rapid oil deterioration.

The use of extreme pressure (EP) additives to assist the lubrication of the heavily loaded gears is subject to limitations, since the majority of such materials do not possess the required thermal stability or are corrosive to the metals with which the oil may come into contact in gas turbine engines.

The low-temperature requirements call for lubricants which change in viscosity as little as possible as temperature is changed (High Viscosity Index) so that an adequate viscosity at high temperatures can be combined with a viscosity at low temperatures not high enough to prevent flow. The lubricant must also remain homogeneous throughout the range of operating temperatures.

In addition, there are other requirements for gas turbine lubricants, namely low volatility, and compatibility with materials of construction. All these requirements are contained in the British Ministry of Supply Specification D.Eng.R.D.2487 and the U.S. Specification MIL-L-7808 for aviation gas turbine lubricants supplied to the Services.

To satisfy the requirements of these specifications it has been necessary to develop new types of lubricant. Conventional mineral oils which have lower viscosity indices than certain synthetic fluids are in practice subject to performance limitations at extremely low temperatures. As is shown later, however, mineral oils should satisfy most low-temperature conditions except the extreme requirements covered by the military specifications mentioned above.

Mineral oils also lack adequate oxidation stability, though in general this can be improved by the use of suitable high-temperature antioxidants except for the most severe conditions encountered in some engines. The load-carrying capacity requirement can be satisfied by choosing an oil of sufficiently high viscosity,

* MS received 16 February 1956. † "Shell" Research Ltd., Thornton Research Centre.

though such oils have inadequate flow characteristics at low temperatures, or else by using suitable EP additives.

In order to meet simultaneously the conflicting requirements, attention has been turned to synthetic lubricants which have been under development during the past ten years or so. The most important classes of such materials include :

(1) Monohydric alcohol esters of dibasic acids, *e.g.* dioctyl sebacate.
(2) Monobasic acid esters of dihydric alcohols, *e.g.* the di-2-ethyl hexoic acid ester of alkylene glycols [and combinations of ester systems (1) and (2)].
(3) Silicate esters, *e.g.* tetra-2-ethyl hexyl silicate.
(4) Ethers of polyalkylene glycols.
(5) Phosphate esters, *e.g.* tricresyl phosphate.
(6) Silicones or polysiloxanes.

Each of these groups of chemical products offers certain advantages with respect to the above-mentioned major requirements—although all have the disadvantage of high cost. To date, diester type lubricants have given the best all round performance. New compounds are, however, continuously being synthesized and claims made for improvements in this or that property.

It is evident that synthetic lubricants are required to meet the current and future demands of military gas turbine engines, but the case for their exclusive use in the civil field, which tends to be guided by military developments, is perhaps less well established.

It is not possible in a paper of this type to deal in detail with all aspects of the problems, hence two of the major requirements have been chosen, namely :

(1) load-carrying capacity, in particular the effect of speed ;
(2) low-temperature performance, in particular work carried out in a cold room on two gas turbine engines.

In the following pages results are presented of work which is being conducted on these topics in the authors' laboratories.

LOAD-CARRYING CAPACITY OF GAS TURBINE LUBRICANTS

When synthetic materials were introduced as potential gas turbine lubricants it immediately became necessary to study their behaviour as gear lubricants. The test machine considered most suitable for such investigations was the IAE 3¼-in centres gear rig, a machine employing the power circulation principle with two pairs of gears connected by two parallel shafts. The machine is run at a constant speed and the load on the gears necessary to cause scuffing of the teeth within five minutes is measured. This machine is specified in D.Eng.R.D.2487 specification as the means of measuring load-carrying capacity.

It was soon found that in general the non-hydrocarbon materials had higher load-carrying capacities than mineral oils of similar viscosity grade. This has meant that the requirements of current engines could be adequately met by the use of selected materials. Should gear loadings outside the range possible with straight synthetics be required in future, then compounding with EP additives will become necessary. This may present some difficulties, for, in addition to the limitations to which reference has already been made in the introduction, the response of synthetic lubricants to EP additives is in general poor, and materials effective in mineral oils are, more often than not, less effective in synthetics. This means that the background knowledge available on the use of materials as EP additives in mineral oils cannot be directly applied to synthetic oils.

Most of the work to study the load-carrying capacity of gas turbine lubricants has been carried out at relatively low speeds not very representative of practice. The U.K. specification calls for tests at a pinion speed in the IAE gear rig of 2000 rev/min (750 ft/min max sliding velocity), whereas reduction gears of propeller turbine engines frequently operate at sliding speeds of 2000–4000 ft/min. Previous investigators [1,2] have claimed that, although the load-carrying capacity of a lubricant decreases as speed is increased, the relative rating of both mineral and synthetic oils at low speeds remains unaltered at high speeds. However, recent tests on an IAE gear rig modified to run at speeds up to 12000 rev/min have shown that at very high speeds some unusual phenomena occur and that predictions of oil performance at high speeds made on the basis of the results of tests at low speeds may be misleading.

Fig 1 shows the comparative performance of three synthetic materials of comparable viscosities tested neat. It will be noted that at a moderate bulk oil temperature and at low speeds lubricant *A* is far superior to both lubricants *B* and *C* (despite the fact that its viscosity (at 210° F) is slightly lower than those of the other two lubricants). As the speed is increased the load-carrying capacity of all three lubricants decreases, but that of lubricant *A* falls so rapidly that it is very soon less than that of lubricant *B*. Over the more practical range of speeds, therefore, lubricant *B* is in fact the best of the three lubricants. At the high bulk oil temperature lubricant *A* is seen to be no better than lubricant *B* at low speeds, and at high speeds it is worse. Thus lubricant *A* is very sensitive to both speed and temperature, and hence cannot be recommended as a gear lubricant in gas turbines. It is obvious, however, that had the materials been compared only at low speeds the limitations of lubricant *A* would not have been realized.

Fig 2 shows the response of a synthetic material of Class 1 to two EP additives. Additive *X*, which is extremely effective at low speeds, is found to be ineffective at high speeds, whereas additive *Y* remains effective over the whole speed range. (This particular additive, however, is unsuitable for gas turbine

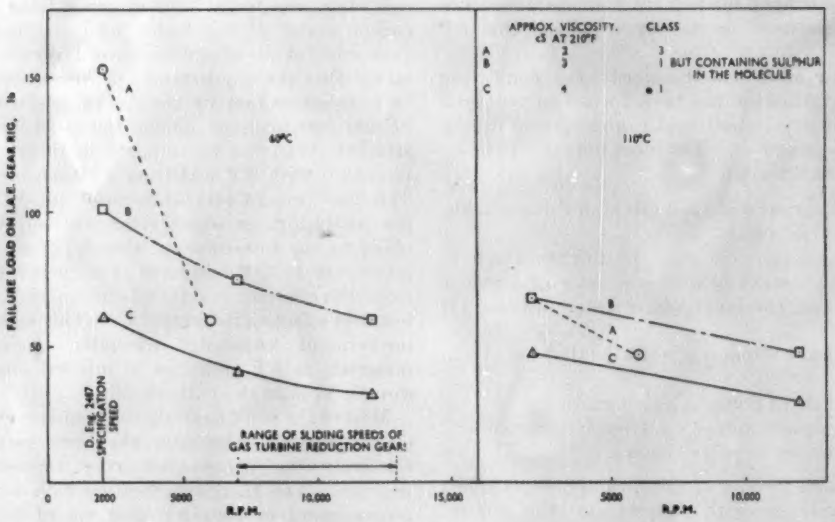

FIG 1

COMPARATIVE LOAD-CARRYING CAPACITY OF THREE SYNTHETIC LUBRICANTS AS AFFECTED BY SPEED AND BY TEMPERATURE

applications because of poor thermal stability and corrosivity.)

The problem of additive response under various operating conditions has not yet been studied in detail. The phenomenon is not confined to synthetic

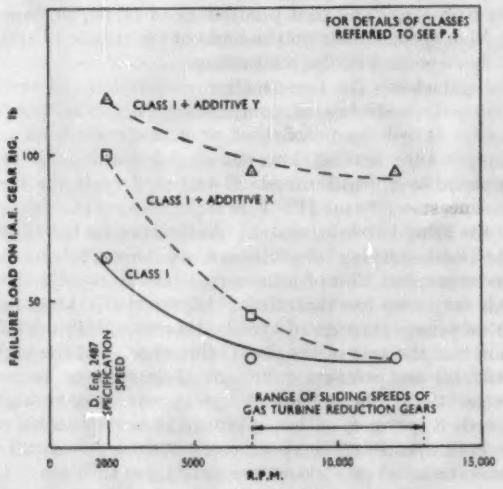

FIG 2

RESPONSE OF A SYNTHETIC LUBRICANT TO TWO EP ADDITIVES

oils—similar behaviour has been observed with additive-type mineral oils. The load-carrying capacity of oils containing additives does not drop below that of the base oil, as might be expected. Some additives continue to function right up to the highest speeds so far tested, *e.g.* additive *Y* in Fig 2), but may cease to be effective at even higher speeds. As yet no reasons for the different behaviour of different lubricants can be advanced, although it is probably connected with the temperatures of the sliding surfaces, the duration of the contact, and the rate of reaction of the additives.

The above results are perhaps sufficient to show that the laboratory development of new gas turbine lubricants must include a comprehensive evaluation of load-carrying capacity over as wide a range of practical conditions as possible.

LOW TEMPERATURE ASPECTS

It has been stated in the introduction that aviation gas turbine lubricants must be able to lubricate bearings at temperatures approaching 280° C, yet must also be able to satisfy the starting requirements of engines at extremely low temperatures. To achieve this objective it would be an advantage if gas turbine lubricants had a constant viscosity over their working temperature range, but unfortunately this cannot be achieved in practice.

Fig 3 shows the viscosities of several mineral and synthetic oils at various temperatures plotted on a standard ASTM chart. It can be seen that the influence of temperature on viscosity for the synthetic oils is less than for the mineral oils, i.e. the viscosity index is higher. The mineral oils are also characterized by a sharp increase in viscosity at low temperatures, this feature being attributed to the formation of a wax crystal structure which resists flow. The synthetic oils, on the other hand, exhibit an approximately straight-line relationship at all temperatures.

From data such as this, it is generally assumed that synthetic oils can be expected to give very much better low-temperature performance than mineral oils in gas turbine engines. However, full-scale engine tests clearly indicate that the low-temperature performance

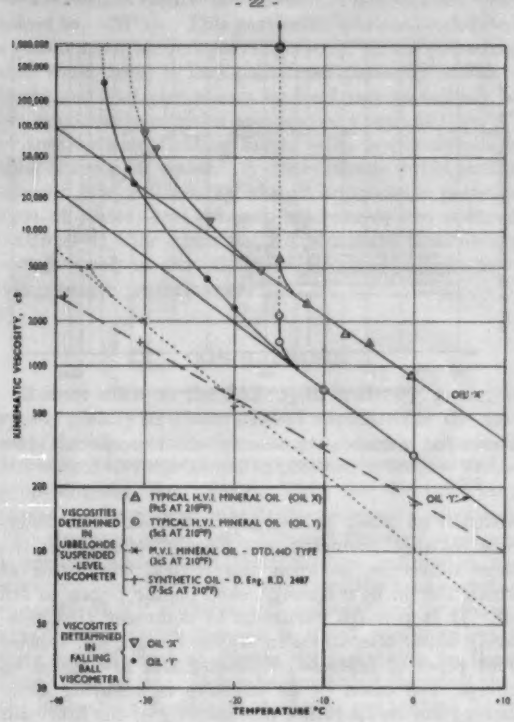
- 22 -
KINEMATIC VISCOSITY, cS
TEMPERATURE °C
OIL 'X'
OIL 'Y'
VISCOSITIES DETERMINED IN UBBELOHDE SUSPENDED-LEVEL VISCOMETER
TYPICAL H.V.I. MINERAL OIL (OIL X) (4cS AT 210°F)
TYPICAL H.V.I. MINERAL OIL (OIL Y) (3cS AT 210°F)
M.V.I. MINERAL OIL - DTD.44D TYPE (3cS AT 210°F)
SYNTHETIC OIL - D. Eng. R.D. 2487 (7·5cS AT 210°F)
VISCOSITIES DETERMINED IN FALLING BALL VISCOMETER
OIL 'X'
OIL 'Y'

FIG 3

VISCOSITY–TEMPERATURE DIAGRAM BASED ON ASTM STANDARD VISCOSITY–TEMPERATURE CHART

of gas turbine oils, particularly the performance of mineral oils, cannot be reliably predicted from a consideration of conventional low-temperature viscosity measurements or from poor point values.

ENGINE CONSIDERATIONS

(*a*) *Starting Torque.* In tests carried out in cold rooms at the Thornton Research Centre, both a modern propeller turbine engine and a modern turbojet engine were motored up to light-up speeds by instrumented electric motors. Several experimental synthetic and mineral oils were tested at temperatures ranging from ambient to −55° C.

In the propeller turbine engine tested, the compressor and turbine blades were removed to eliminate aerodynamic factors. Measurements were then made of the torque required to accelerate this engine up to its light-up speed at different temperatures when using a typical high-viscosity index gas turbine oil (oil *X* in Fig 3).

In attempting to establish a relationship between torque requirement and oil viscosity, it was found that the torque values obtained could be related to the square root of the oil viscosity at the operating temperature, provided that the viscosity values used were obtained by linear extrapolation on the ASTM chart and not determined in conventional viscosity-measuring apparatus at these temperatures. Fig 4 shows the relationship obtained.

It is interesting to note the similarity between these observations and published information on the starting characteristics of piston engines. In a large number of tests on many types of automotive engine, Barrington and Lutwyche [3] have shown that the cranking torque $T = K\sqrt{NV}$, where N is the cranking speed (rev/min) and V is the oil viscosity expressed in absolute units. Arter,[4] who confirms that cranking torque can be related to the square-root of the oil viscosity, suggests that extrapolated viscosity values are more appropriate to starting conditions in piston engines than are actual viscosity values measured at low temperatures.

With the other gas turbine engine, similar effects were observed; for instance, it proved possible to start and accelerate this engine with oil *Y* at −42° C, a temperature which (see Fig 3) is well below the value at which the measured viscosity values rise abruptly. This operating temperature is also considerably below the pour point of the oil. With this engine, which in this case was complete with compressor and turbine blading, the observed amount of electrical energy used by the starter motor to start and accelerate the engine up to its light-up speed using oil *Y* was only 50 per cent greater at −42° C than at +10° C.

It was concluded from this work that oil viscosity is a major factor influencing the starting torque requirements of gas turbine engines and, in the case of mineral oils, the extrapolated viscosity is more realistic than the measured value.

An explanation why the operating viscosities of mineral oils conform to the extrapolated straight-line values can be seen by referring again to Fig 3. In this figure a series of viscosities for oil *X* has been plotted which were obtained using a falling-ball viscometer in place of the conventional suspended-level capillary (Ubbelohde) type. The shear forces occurring in the falling-ball viscometer, although relatively small, are nevertheless greater than those which arise in the Ubbelohde apparatus, and it will be noticed that the viscosity values obtained show a marked tendency to approach the straight-line relationship. At the much higher shear-rates which occur in the bearings of gas turbine engines it appears reasonable to expect that the operating viscosities of mineral oils will approximate to the straight-line extrapolated values.

Attempts were made on both engines to observe whether the torque requirements at the instant of starting, *i.e.* when the shear-rates are momentarily

low, were disproportionately higher for mineral oils; although many measurements were made, no evidence of such an effect could be discerned.

(*b*) *Oil circulation.* Another important aspect of low temperature performance is the ability of the lubricant to flow to the bearings and gears and then lubricate them.

Most gas turbines use one main gear pump to feed the lubricant to the different parts of the engine. Sometimes the lubricant is fed to the bearings on a total-loss system, but more often the oil is circulated back to the oil sump by means of scavenge pumps; these again are usually of the gear type.

An examination of the rate of oil flow through the main oil pump on the two engines, for both synthetic and mineral oils, has shown that, at each pump speed, the pump output is sensibly constant until the viscosity of the oil rises to a value above which flow into the gear-pump teeth is restricted.

At viscosities above this critical value (which varies with the pump speed) the flow through the pump becomes inversely proportional to the operating viscosity, *i.e.* the flow through the pump is then governed by inlet considerations, which follow Poiseuille's law. Fig 5 shows how the low-temperature pumpabilities of a number of mineral and synthetic oils were found to be related to their extrapolated straight-line viscosities, for one of the engines.

In both engines it was possible to record adequate oil flow through the main oil pump with mineral oils at temperatures well below their pour points, thus demonstrating once again how pour points and conventionally measured low-temperature viscosities

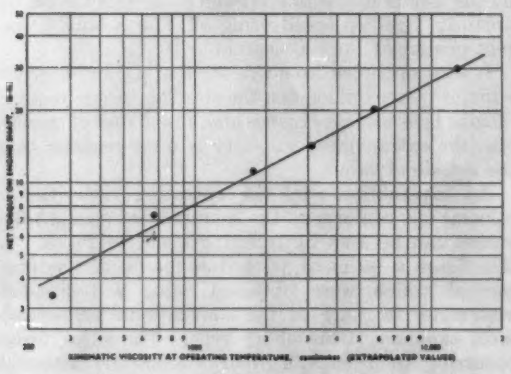

FIG 4

VARIATION OF ACCELERATING TORQUE WITH VISCOSITY

are liable to give a completely erroneous indication of the low-temperature limitations of mineral oils.

In addition to measuring oil flow through the main oil pump, the use of sight-bottles in the scavenge lines enabled observations to be made of the amount of oil being returned to the sump from the various feed lines. In all the tests carried out, satisfactory scavenge line operation was experienced until the main oil pump output became appreciably depleted.

An interesting observation made during these tests was that oils performed very much better in one engine than in the other (Fig 4 refers to the worst engine). The reasons for this can be attributed to design factors; in the engine which gave the inferior oil performance a separate oil tank is used, whereas in the other the oil sump is an integral part of the engine

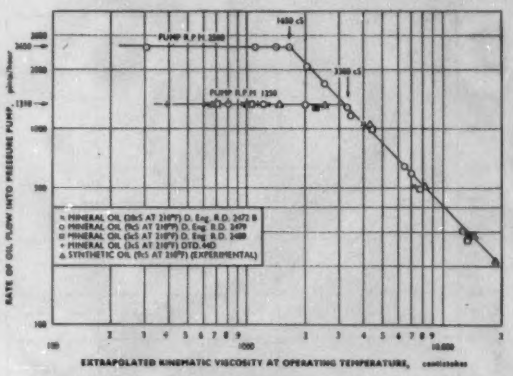

FIG 5

EFFECT OF OPERATING VISCOSITY ON ENGINE OIL FLOW CHARACTERISTICS WITH VARIOUS SYNTHETIC AND MINERAL OILS

with the oil pump submerged in the oil. The difference in inlet geometry was clearly reflected in the large difference between the critical viscosities at which the oil flow through each engine began to fall off. It is perhaps pertinent to comment that relatively small alterations in engine design, *e.g.* shorter inlet pipes of increased diameter and low speed oil pumps, can often be as effective in ensuring satisfactory low-temperature pumpability of the lubricant as a change from a mineral to a synthetic oil.

GENERAL

The cold room tests which have been carried out have indicated that the best criterion for comparing the low-temperature performance of gas turbine lubricants is the "operating" viscosity, which in the case of mineral oils approximates to the straight-line extrapolated value.

If the low-temperature viscosity limitations of a particular engine are known, it is therefore a relatively straightforward matter to select lubricants to meet specific low-temperature engine requirements. It also appears that the lowest operating temperature for mineral oils may be lower than has hitherto been supposed, and that proper design of lubricating oil systems can also extend the useful range of such oils.

In the course of this low-temperature work some additional observations were made concerning the behaviour of synthetic oils which are worth recording.

Unlike mineral oils, where the transition from a liquid to a solid (and vice versa) is gradual and the nature of the solid is more akin to a stiff paste or grease,

some synthetic lubricants have been found to solidify over a relatively short range of temperatures to crystalline masses which are somewhat difficult to melt completely on heating. One synthetic lubricant was found to solidify in an engine when left for several days at −48° C, and, furthermore, did not allow flow to commence until the ambient temperature was raised to −30° C. This particular lubricant exhibited a pronounced tendency to supercool; in the preceding cold room tests it had performed perfectly satisfactorily and had also shown no tendency to solidify in conventional pour point and viscosity tests at −60° C.

Another complicating factor with synthetic oils is their affinity for water. Some synthetic fluids, unlike mineral oils, will readily absorb appreciable percentages of water, and when temperatures are reduced below 0° C this forms an ice structure (resembling cotton wool) in the oil which adversely affects low-temperature performance.

CONCLUSIONS

Recent work on the IAE 3½-in centres gear rig, at speeds greatly in excess of that stipulated in the current British specification for gas turbine lubricants but nearer to those found in practice in certain turboprop engines, has shown that the load-carrying capacity of synthetic lubricants decreases with speed. This decrease varies with different types of synthetic lubricants and affects their relative ratings at the various speeds tested. In addition, the load-carrying capacity of EP additive oils, mineral and synthetic, also decreases with increase in speed, and may reach the base oil level at speeds corresponding to those found in practice. It can be concluded therefore that the laboratory development of new gas turbine lubricants must include a more comprehensive evaluation of load-carrying capacity than is demanded for the purpose of meeting current specification requirements.

Low-temperature studies on mineral and synthetic oils on two current gas turbine engines in the cold room have shown that oil viscosity is a major factor influencing both the starting torque requirements and low-temperature pumpability of these engines and that the pertinent viscosity in the case of mineral oils approximates to the extrapolated and not the measured value. Thus mineral oils, though showing some low-temperature limitations for use in gas turbines, are not so bad as their pour points would indicate, and should give perfectly satisfactory performance in suitably designed engines where the minimum oil temperatures are not appreciably lower than −30° C.

To meet extreme low-temperature requirements, in the region of −50° C, which may possibly arise in military aircraft in very cold areas, synthetic lubricants have to be used. Their choice must, however, be governed by a very careful study of their true low-temperature characteristics.

ACKNOWLEDGMENTS

The Authors wish to thank the Directors of "Shell" Research Ltd. for permission to publish this paper. They also acknowledge their indebtedness to colleagues who have helped in the experimental work which has been described.

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[2] Hughes, J. R., and Tourret, R. *Engineering*, 1953, **175**, 200–3 and 257–9.
[3] Barrington, R., and Lutwyche, J. L., *Proc. Instn. Mech. Engrs, Lond.*, 1937, **1**, 400.
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DISCUSSION

B. E. Hurley: During the last IP Symposium on Gear Lubrication,* there was obviously an incompatibility of outlook between papers, some showing that hydrodynamic fluid film lubrication was the main mechanism involved, and the remainder postulating that surface effects were the most important. There is a school of thought which suggests that in the region at the bottom of the μ (coefficient of friction)/ZDN (viscosity × peripherical speed) curve the film of lubricant behaves in a physically, but not necessarily chemically, different manner from the normal bulk properties. This "physical" effect would be more likely to be related to molecular length than to surface properties.

Since a natural petroleum lubricant is a mixed bag of many thousand compounds, no real determination of the relative merits is possible. In the case of synthetic lubricants the material is approximately chemically homogeneous, and the surface properties and molecular length are actual and not averages.

Which of these properties correlates with the observed phenomena shown in Fig 1?

R. Tourret: The results presented in Figs 1 and 2, showing the comparative load-carrying capacity of lubricants as affected by speed, are of particular interest. Similar results (Fig A) were obtained a year or two ago in an Admiralty-sponsored series of tests conducted by Shell and Esso. Both sets of results indicate that the early suggestion † that the relative rating of different lubricants remained the same irrespective of the speed is not necessarily generally applicable. The theory then presented presumably remains true for undoped oils, and perhaps also for a limited number of additives.

It is suggested that the speed of reaction of E.P. additives with the gear material to form protective surfaces may not always be the same, and hence the speed of rotation affects the order of merit of different lubricants. Reference is made to bulk oil temperature,

* *J. Inst. Petrol.*, 1952, **38**, 606–804.
† Hughes, J. R., and Tourret, R. *Engineering*, 1953, **175**, 200–3, 257–9; Greenwood, J., and Morton, R. W. *J. Inst. Petrol.*, 1952, **38**, 732.

but the temperature which will affect the speed of reaction most is probably that in the reaction zone, i.e. the contact zone. Little is known about the magnitude of this temperature, but it is fairly certain at least that (1) it bears little relation to the bulk oil temperature, and (2) it is much higher than the bulk oil temperature. Naturally, the speed of reaction will be increased by increased temperature and, in turn, the contact temperature will be increased by both high sliding speeds and high loadings. Hence, it may be surmised that load as well as speed will affect the speed of reaction of additives, and hence the relative order of merit of lubricants in which they are incorporated.

It follows if high speeds and high loads are both conducive to increased additive activity that, since high loads normally go hand-in-hand with low speeds and vice versa (*e.g.* Figs 1 and 2 of the paper and Fig A of this contribution), a given additive may give its best relative performance at high speed when used with one set of gears and at low speed when used with another different set of gears. Further, in some applications the speed effect may more or less balance the load effect, and the doped oil will then behave as an undoped oil in so far as it will not give a different relative performance at different speeds.

It was interesting to learn from V. W. David's disclosure during the discussion following the presentation of the paper that Additive X in Fig 2 was tricresyl phosphate. The explanation why, in one series of tests in the Thornton high-speed gear rig (a modified IAE 5-inch centres gear rig), tricresyl phosphate did not change its relative order of merit, whereas in the present series of tests (Fig 2) in an IAE 3¼-inch centres gear rig its relative performance dropped with increase of speed, may be that advanced in the previous paragraphs. There are other factors involved, such as amount of additive present in the blend, and other explanations may be applicable.

V. W. David, J. R. Hughes, and D. Reece: In presenting the paper we stressed that the results so far obtained on the influence of speed on the load-carrying capacity of lubricants were considered to be of interest, but not in themselves sufficient to enable any generalizations to be made nor for any convincing explanation of the observed phenomena to be given. We regret, therefore, that we do not feel justified in attempting to answer Mr Hurley's question.

In reply to the point concerning the effect of temperature on the performance of E.P. additives at different gear speeds, it might be expected that by increasing the bulk oil temperature E.P. additives would become more reactive, so that the speed at which additives cease to be effective would increase with increasing bulk oil temperature. However, limited work so far has shown that, with some materials at least, the speed at which additives cease to be effective decreases with increasing bulk oil temperature, although at this stage of the work we would not wish to generalize from this finding.

Mr Tourret's subsequent argument regarding the influence of load is difficult to follow. Since in most gear tests the load at failure is itself the criterion of oil performance, it can, therefore, hardly influence the order of rating of lubricants.

One major difference between the two series of tests on tricresyl phosphate lies in the base oils, synthetic in the present series, mineral in the previous. It is considered that this is a more likely reason for the difference in behaviour of the additive in the two series than Mr Tourret's suggestion of a load–speed interaction.

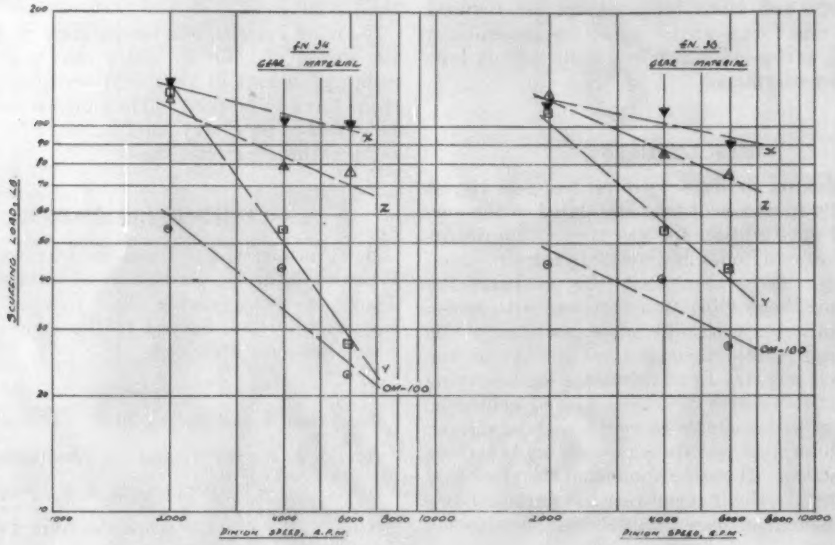


FIG A

LUBRICANT ADDITIVES AND THEIR ACTION *

By C. V. SMALHEER and T. W. MASTIN †

SUMMARY

The history of the commercial development of hypoid gear lubricants and heavy-duty detergent oils in the U.S.A. is discussed, with particular reference to the important role played by full-scale test procedures in this development.

Two distinctly different kinds of boundary lubrication have been observed, each of which requires the use of a particular type of improving agent or "additive." Under service conditions where both kinds of boundary lubrication are encountered, there is evidence that some additives reduce or negate the effectiveness of other additives present in the lubricant.

Substantially all present-day heavy duty detergent oils contain a "basically-reacting" detergent additive to minimize corrosive wear of the engine parts. The chemistry and mode of action of this important type of detergent additive are considered.

In its broadest sense, the term "lubricant" applies to any material—liquid, gas, or solid—which has the property of reducing friction and wear between relatively moving surfaces. The present discussion is confined to mineral oil base lubricants and the "additives" used to improve their properties.

A lubricant additive may be defined as a material used (*a*) to impart to a lubricant a new and desirable property not originally present to any significant extent; or (*b*) to reinforce a property of the original lubricant.

Historically, the first use of chemical compounds as lubricant additives dates back to about the middle of the nineteenth century, when Raecz [1] and Little [2] proposed admixing petroleum oils and fatty acid soaps to produce lubricating greases.

With the advent of motor vehicles at the end of the nineteenth century, lubrication problems arose which were not met satisfactorily by plain mineral oils, solid fats, or fatty oils. For example, the need for lubricating greases which would not become rancid and corrosive towards metal surfaces was met by the use of mineral oils thickened with fatty acid soaps in the manner proposed by Raecz and Little.

Succeeding years have seen the growing use of a wide variety of chemicals as additives, as continuing advances in engine and gear design have placed increasingly severe demands on lubricants, demands which are not met satisfactorily by uncompounded mineral oils.

A number of familiar terms are used in the trade such as detergent, dispersant, antioxidant, anti-corrosion agent, extreme-pressure or "EP" agent, viscosity index or "VI" improver, to describe different types of additive materials.

During the past decade, important improvements have also been made in additive-treated lubricants, hypoid gears, automatic transmissions, and high-powered diesel equipment. While these improved lubricants have provided a practical solution for many special and difficult lubrication problems just as real as those encountered in the overhead valve engine, the knowledge of their development and application has scarcely gone beyond those directly concerned with the problems involved.

Thus, it is worthwhile to analyse the close liaison between the petroleum and additive industries and the equipment manufacturers in the U.S.A. When certain lubrication problems arise due to advances in equipment, power, and design, they are generally brought to the attention of those in the lubrication industry. Efforts are then made to solve the problems before the improved equipment reaches the market. When full-scale laboratory and field tests have convinced the equipment manufacturer that the lubricant is capable of giving satisfactory service, he may place a formal approval on the lubricant. In some instances, he may even designate a "part number" for the lubricant just as he would for a mechanical component of the equipment.

In an ideal circumstance, the consumer will obtain satisfactory lubrication for his equipment with little or no knowledge of the special performance qualities of the lubricant. However, such an ideal situation is not always realized, and shortcomings may arise in the field, reports of which reach the equipment manufacturer who attempts to determine if a deficiency exists in mechanical design or in lubrication. If it is the latter, the problem will again be discussed with the petroleum and additive industries. Co-operative research will then seek a practical solution in the shortest possible time.

This close liaison has also done much in the past decade to make available effective lubricant testing techniques, with ever-increasing emphasis on data gathered from full-scale tests. The increasing complexity and severity of the lubrication requirements of the modern motor emphasizes the necessity for such tests.

Consider the lubrication and stability requirements of an automatic transmission of the clutch and gear design. Satisfactory lubrication requires a certain degree of several additive-conferred properties such as oiliness, non-corrosiveness, oxidation stability, extreme-pressure resistance, detergency, or dispersance, and even a few, such as the ability to prevent

* MS received December 1955.

† The Lubrizol Corporation, Cleveland, Ohio.

"squawking" noise, for which no classical definition exists. An attempt to solve such a complex lubrication problem by means of laboratory bench test devices, each measuring a particular property in a restricted operating environment, might succeed, but only after years of intensive research. Through the use of full-scale laboratory test equipment employing factory-built commercial units, complemented by actual service tests on proving grounds and in the field, effective lubricants were made available in less than one year.

Additives are materials which can best be classified according to the tasks they are to perform and how well they perform them. Evaluation of performance ability is inseparably joined with the test techniques employed. An evaluation based on data gathered from bench test devices is one thing, and an evaluation based on tests in full-scale equipment is another and, generally, a different thing.

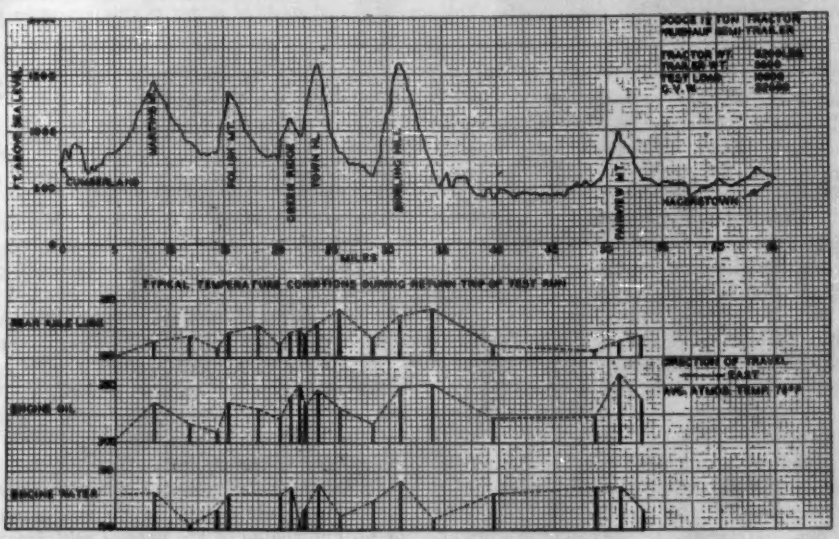


FIG 1

ROAD CONTOUR FOR MOUNTAIN TRUCK TESTS

U.S. route 40 between Cumberland and Hagerstown, Md.

BENCH TESTS OF ADDITIVES

Even though each succeeding year brings with it a greater reliance and confidence in full-scale equipment tests, there is no doubt that bench test devices such as film strength machines, bench detergency tests, and the like have a useful role in furthering the science of lubrication. Their proper role is limited, however, to areas of: (*a*) fundamental studies dealing with laws governing lubrication in the hydrodynamic, quasi-hydrodynamic, and boundary regions of lubrication; (*b*) theories and mechanisms to explain the behaviour of additive materials, and (*c*) "screen" tests, where a useful degree of correlation has been established with full-scale tests. A review of the literature clearly indicates that many important contributions in these areas of endeavour have been made possible through the use of bench test devices.

Much useful information as to the action of lubricant additives can be gleaned also from the many excellent papers and monographs published in the past thirty years.

The so-called extreme-pressure (EP) lubricants are used principally to prevent destructive metal-to-metal contact between relatively moving gear surfaces, particularly those of hypoid gears. As suggested by Bowden and Tabor,[3] such lubricants might more accurately be termed "extreme-temperature" lubricants, since pressure per unit area on the actual contacting surface asperities presumably does not change with loading. Rather, the increased pressures result in increased contact areas. As a result, forces greater by an amount proportional to the increased contact area must be applied to overcome friction. Much of the energy expended in overcoming friction is, of course, converted into heat.

Experiments by Bowden and Ridler,[4] employing a metal cylinder sliding over the surface of a dissimilar metal, have shown that local temperatures may rise as high as 1100° F on lubricated surfaces. In actual practice, these high local temperatures are rapidly distributed through the body of the lubricant and the metal parts, resulting in substantially lower overall temperatures. Bulk lubricant temperatures in the hypoid gear units of heavily loaded trucks operating in mountainous areas of the U.S.A. have been shown to lie in the range 190°–265° F (see Fig 1). In these field test studies the observed temperatures were

noticed to vary principally according to the kind of lubricant used, the hours of service on the hypoid gears, and the particular terrain traversed.

The discussion above serves to establish that very substantial thermal forces come into play in EP lubrication.

Prutton *et al* [5] and Musgrave [6] have reported that EP additives are principally lead or other heavy metal soaps and organic compounds of sulphur, chlorine, and phosphorus used in various combinations. Although the specific mode of action of such additives will obviously vary according to their chemical composition, numerous investigators [7] are in substantial agreement that an EP additive reacts chemically with the metal of the gear surface under boundary conditions to form a tenacious solid film which has a lower shear strength than the metal itself and which acts as the boundary lubricant. There is no appreciable formation of this film at ordinary temperatures. It forms only at the elevated temperatures which have been shown to exist under boundary lubrication conditions. Greenhill [8] has quite appropriately termed this phenomenon a sort of "controlled corrosion" where thermal energy determines the extent of chemical reaction, *i.e.* "corrosion."

In this connexion, the actual formation of metallic lead, iron chlorides, and iron sulphides by the reaction, respectively, of lead soaps, organic chloride compounds, and organic sulphur compounds with iron has been observed by Simard *et al* [7] and Prutton *et al*.[7] Indirect evidence of the formation of boundary lubricant films is also contained in the studies of Thorpe *et al*,[9] who found that the electrical contact resistance of a 1 per cent mineral oil solution of tricresyl phosphate was very high when measured under boundary conditions in the four-ball machine. This observation was interpreted to indicate that metal-to-metal contact was small, presumably owing to the presence of a solid, poorly conducting film on the steel balls.

FIELD TESTS OF ADDITIVES

Although experiments carried out on lubricants in bench test devices may contribute useful information, an actual lubrication problem is best resolved by trying something in an environment like that where the problem is observed to exist. This might be termed a direct approach in that it does not entail extrapolation of test results from one test device to another. In terms of test equipment, this means a liberal use of full-scale equipment in the laboratory and in the field. In terms of additives and combinations of additives the initial selection may be based on those materials which experience indicates will confer the performance characteristics believed to be required.

If the initial programme of testing has been carefully laid out, certain trends will be indicated which make the subsequent selection of additives rather apparent. Improvement of test results can thus be realized until the ultimate answer is obtained.

The earliest successful lubricant for hypoid gears contained a lead soap and "active sulphur." The latter term is used to designate a sulphur-bearing organic material in which a substantial portion of the sulphur is in loosely combined or labile form and is therefore capable of reacting with metals such as iron or copper to produce metal sulphide coatings.

Towards the end of the 'thirties, hypoid lubricants containing chlorine and relatively less active sulphur, either in single or separate organic molecules, were developed and sold commercially. These lubricants gave satisfactory performance in service and provided certain advantages over their lead soap–active sulphur predecessors, principally with respect to improved solubility and reduced corrosion of the copper or copper alloy parts in hypoid gear rear axle assemblies.

The chlorine–sulphur type of hypoid lubricant constituted by far the major portion of all gear lubricants sold in the U.S.A. for both military and civilian needs through the period ending with the close of the second world war.

Throughout this period, the only full-scale performance requirement for military acceptance of a finished hypoid lubricant was that it should prevent damage to hypoid gears in the test [10] wherein a series of sudden or "shock" loads were applied at high speeds. Although bench devices such as the familiar Timken, Almen, Faville–Levally ("Falex"), and SAE EP lubricant testers were valuable as so-called "screen" or "selection" tests to weed out grossly inadequate lubricants, they were not capable of predicting which of the "screened" lubricants would pass the full-scale shock test.

Towards the close of the second world war the Ordnance Department of the U.S. Army, drawing both from its wide field experience and from the work of the CRC, issued a new gear lubricant specification [11] which called for two full-scale hypoid gear tests. One test, called a "high-speed axle test," was to be run at high speeds and low torque and the other, called a "high-torque axle test," was to be run at low speeds and high torque. This new specification, which was promptly adopted by the petroleum industry as a criterion for gear lubricants destined for the civilian market as well as the military, gave a decided impetus to full-scale test research. No bench device or combination of bench devices proved adequate to predict the performance of a lubricant in both of these tests. It appeared that the new tests segregated and evaluated different aspects of boundary lubrication which could not be differentiated by existing bench devices. Although continued work has shown a limited degree of correlation between a few bench test devices and the high-speed axle test, enabling the elimination of inferior lubricants, no bench device has yet been found which will predict the performance of lubricants in the high-torque axle test.

Lead soap–active sulphur and chlorine–sulphur hypoid lubricants, while they often gave satisfactory performance in the high-speed axle test, invariably failed to pass the severe high-torque test which speci-

fied operation for 30 hr under a ring gear torque of 32,311 inch-pounds.

This new specification called for an improved lubricant which—even in the initial stages—could be developed only through the medium of full-scale test equipment. It also contained a number of strict requirements relative to characteristics such as thermal stability, permanent oil solubility, non-corrosiveness, sulphur activity, etc. Requirements of this kind greatly reduce the number of "candidate" additives, and thereby further complicate the task of developing a satisfactory lubricant.

The lead soap–active sulphur and chlorine–sulphur lubricants were satisfactory for the high-speed type of operation, but were almost completely ineffective under high-torque conditions of operation. The answer, therefore, appeared to be quite obvious. A series of high-torque tests should serve to segregate additives which are effective in this test, and any of these, upon addition to a chlorine–sulphur lubricant, should provide a lubricant giving satisfactory performance in both tests.

However, it was found that the addition of additives of proved effectiveness in the high-torque test of an existing chlorine–sulphur lubricant only provided a lubricant which would pass the high speed, but not the high-torque test, or vice versa.

Here, then, a situation must exist where the individual additives were incompatible in a performance sense, *i.e.* helping in one of the tests, but negating or reducing the effectiveness of a companion additive in the remaining test.

In view of this, it seemed necessary to collect some fundamental information about the full-scale high-speed and high-torque performance characteristics of a wide variety of additive materials. Using data acquired in these studies, a selection of the most promising "building blocks" for the lubricant could then be made.

Full-scale tests on a large number of organic compounds indicated that each could be classified in one of the following six groups:

(i) not helpful in either test;
(ii) helpful in both tests;
(iii) helpful in high-speed operation, but harmful in high-torque operation;
(iv) helpful in high-torque operation, but harmful in high-speed operation;
(v) helpful in high-speed operation, but ineffective in high-torque operation;
(vi) helpful in high-torque operation, but ineffective in high-speed operation.

Table I gives the performance characteristics of a number of families of organic compounds in full-scale test equipment studies. Not all the members of these families could be tested, but several specific members of each family were tested and form the basis for the conclusions. Although there are exceptions to the generalizations noted in the table, it is believed, nevertheless, that they are quite reliable on a "rule of the thumb" basis.

TABLE I

Key: + = definitely effective.
(+) = slightly effective.
0 = ineffective, but not harmful.
(−) = slightly harmful.
− = definitely harmful.

Family of compounds	Use in hypoid gear service under conditions of:	
	High speed	High torque
Chlorine bearing	+	0 to (+)
Active sulphur in non-carboxylic compound	+	−
Relatively inactive sulphur in non-carboxylic compound	+	(−)
Relatively inactive sulphur in carboxylic ester	(−) to (+)	+
Relatively inactive sulphur in carboxylic acid	+	+
Carboxylic esters	−	+
Carboxylic acids	(−) to −	+
Oxyphosphite acid esters	+	+
Oxyphosphite neutral esters	0	0
Oxyphosphate neutral esters	0	0
Thiophosphate neutral esters	+	+

Having these data, a lubricant was compounded which:

(i) would pass both the high-speed and high-torque tests;
(ii) was satisfactory from the standpoint of permanent oil solubility, non-corrosiveness, and stability at elevated temperatures, and
(iii) presented no undue difficulties in large-scale manufacture and could be sold on a sound economic basis in a competitive market.

If satisfactory performance in the high-speed test and the high-torque test were the only criteria, it would be very easy, of course, to compound a suitable hypoid lubricant using only additives selected from "compatible performance" groups, *i.e.* groups which showed no harmful effect in either test.

However, since the requirements enumerated in (ii) and (iii) above relative to stability and cost must also be met, a compromise between additives from both compatible and incompatible performance groups may be the more usual end result. Additional full-scale tests of lubricants containing additives from both compatible and incompatible performance groups demonstrated that additives belonging to the latter group can be successfully employed, provided that their concentration in the lubricant does not exceed certain rather critical values above which the incompatible performance characteristics become pronounced and objectionable.

The concept of two distinctly different kinds of EP lubrication and the phenomena of incompatible performance characteristics are not generally known and appreciated. These subjects might well form the

basis for interesting fundamental studies in the realm of boundary lubrication.

DETERGENT ADDITIVES

In direct contrast to the impressive amount of research carried out in the field of boundary lubrication, there has been relatively little reported in the way of fundamental studies of " detergent " or " dispersant " lubricants and their mode of action. This is not to say that detergent lubricants have not been developed to a high degree of effectiveness, which would definitely be untrue. Rather, the situation is a good example of one where progress in the art has far preceded the gathering of fundamental knowledge.

" Dispersant " is perhaps a more appropriate adjective than " detergent " to describe the function of these lubricants. The more widely used varieties do not remove existing deposits from engines, as the term " detergent " might suggest. However, the term " detergent " is generally accepted in the trade.

It would be beyond the intended scope of the present paper to attempt to recount the history of all of the many types of detergent additives which have been used commercially in the U.S.A. for the preparation of various grades of detergent oils since the first detergent oil containing aluminium dinaphthenate was introduced in 1935. A reasonably complete listing of the general chemical classes of detergent additives of proved effectiveness known to be widely used in the U.S.A. at the present writing would include the following:

Normal and basic metal salts of " mahogany " acids, *i.e.* preferentially oil-soluble sulphonic acids derived from petroleum.

Normal and basic metal salts of high alkyl-substituted benzene sulphonic acids.

Normal and basic metal phenates of alkylphenols, alkylphenol sulphides, and alkylphenol–aldehyde condensation products.

Metal salts of acidic materials obtained by partially hydrolysing the reaction products of polyolefins such as polybutene and phosphorus sulphides.

Many detergent additives belonging to chemical families other than the above have been investigated. Some, such as aluminum naphthenate, calcium dichlorstearate, and calcium chlorphenyl stearate, were used commercially in early detergent oils, but have since been superseded by less costly and more effective additives. Others never progressed beyond the laboratory stage for one or more reasons, such as unsatisfactory performance characteristics, high cost, or inadequate supplies of necessary raw materials. Still others have been or are currently being offered on the market, but have not yet achieved wide acceptance. Included within this last group are certain newcomers to the scene, such as a type of so-called " ashless," *i.e.* metal-free, detergent made by copolymerizing lauryl methacrylate with diethylaminoethyl methacrylate.[12] Informative reviews of the detergent additive field are available.[13–19]

No discussion of modern detergent oils would be complete without emphasizing the important role played by " basic " or " basically-reacting " detergent additives. The term " basically-reacting " as here used applies to any detergent additive which assumes the characteristics of a base in neutralizing acidic bodies such as petroleum oxyacids, hydro-halogenic, and sulphur acids. These acidic bodies are present in used crankcase oils as a consequence of their contamination with oil oxidation products and " blow-by " fuel combustion products. Thus, any additive which is capable of neutralizing these acidic contaminants under the conditions encountered in actual engine operation will be considered as being basically-reacting.

In a review of the chemistry and behaviour of this important class of detergent additives, frequent reference must be made to the patent literature because it constitutes the principal and often the only published source of information on the subject.

Aluminum dinaphthenate was the first basically-reacting detergent additive to be employed commercially. Denison *et al* [20] have excellently analysed the matter of the relative basicity of basically-reacting detergent additives such as aluminum dinaphthenate towards petroleum oxyacids. Denison says in part: " If . . . extrapolation from aqueous to lubricating oil solutions could be made, then anti-ring-sticking soaps would necessarily have to be made from acids weaker than oxyacids. However, this is not infallibly the case, nor should the acidity and basicity order be always the same in water as it is in oil. The fundamental test of the operability of these reactions, *i.e.* neutralization of oxy-acids by the detergent additive, in the absence of a knowledge of acidity in oil solutions is—can the reactions be made to take place, for example, in glass [vessels]? " Convincing experimental data are presented to show that oils containing aluminum dinaphthenate can neutralize petroleum oxyacids *in vitro*.

Next to appear on the commercial scene were the normal and basic alkaline earth metal phenates of alkylphenols and alkylphenol sulphide,[21] which remain today as an important class of basically-reacting detergent additives.

The true basic character of phenate additives requires little explanation to the chemist, since phenates have long been recognized as being substantially as basic as the metal hydroxides or oxides from which they are generally made. Thus, it is not surprising that phenates are capable of neutralizing petroleum oxyacids and other acidic contaminants found in lubricating oils. Titration studies carried out on a phenate treated lubricating oil before and after a full-scale engine test show a significant loss in basic titre of the lubricant after service in the engine (Table II). The neutralization of the phenate additive by acidic contaminants is believed to be the principal reason for the observed reduction in basicity.

Some explanation is believed to be in order regarding the terms " normal " and " basic " as applied to phenates, since these terms are not found in textbooks dealing with the chemistry of phenates.

TABLE II

Neutralization Number Before and After a 50-hr Single-cylinder Diesel Engine Test on a Lubricant Consisting of SAE 30 Grade Mineral Oil Plus 2·56 per cent by Weight of the Barium Phenate of a High-molecular-weight Alkylphenol

	Neutralization no. in terms of mg of KOH per gram of lubricant using phenolphthalein indicator
Before test	2·54 basic titre
After test	1·22 acidic titre

The term " normal " phenate is meant to designate a classical phenate in which the normal valence bonds of the metal are satisfied by attachment only to phenolic radicals. Such a phenate would possess the general structure $(Ar–O–)_xM$, wherein Ar–O– is a phenolic radical and x is the valence of the metal M.

McNab *et al* [22] reported that " basic " phenates containing up to two or three times as much metal as the normal phenate can be prepared by reacting alkylphenols or alkylphenol sulphides with an excess of a suitable metal oxide or hydroxide at an elevated temperature. For the basic phenates of alkylphenol sulphides containing, respectively, two and three times the stoichiometric amount of metal they postulate the structures A and B shown in Fig 2.

Very little exact knowledge is available concerning the structure of basic phenates. It is possible that they may consist of colloidal dispersions of metal

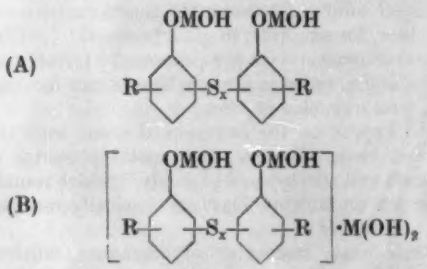


FIG 2

POSTULATED STRUCTURES OF BASIC PHENATE SULPHIDES

Key: M = a divalent metal such as, *e.g.* barium.
R = a long chain alkyl radical.
x = 1 or 2.

oxide or hydroxide in the normal phenate rather than the specific structures A and B suggested above.

The question might be asked as to why efforts should be directed towards the manufacture and use of basic phenates, since normal phenates, which are indisputably basic in nature, would presumably perform the same function of neutralizing acidic contaminants.

The answer lies at least in part in the fact that basic phenates obviously possess substantially greater neutralization capacity per unit weight than do normal phenates. The cost advantage of basic phenates over normal phenates is believed to be quite evident.

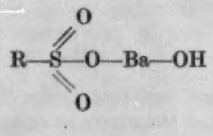
Another class of basically-reacting detergent additives used widely in modern detergent oils consists of the " basic " salts of high molecular weight sulphonic acids, principally those derived from petroleum oils, and long chain alkyl-substituted benzenes.

" Normal " sulphonates, *i.e.* those containing the stoichiometric amount of metal for the classical sulphonate structure $R–SO_3M$, have been used extensively in detergent oils since about 1940.

More recently, Mertes [23] reported that an oil-soluble " normal " metal petroleum sulphonate is capable of " solubilizing " or peptizing substantial amounts of inorganic base such as metal oxide or hydroxide by " . . . a more or less simple mixing and heating operation followed by filtering." He believed, together with Campbell *et al*,[24] that the resulting " basic " sulphonate was most likely a colloidal suspension of the metal base in the oil-soluble sulphonate. His reasons for so believing were that oil solutions of a basic sulphonate exhibit the Tyndall effect and that the number of mols of base incorporated per mol of sulphonate could be made larger than would normally be expected for any new type of complex other than a loose addition compound.

Mertes observed that the basic sulphonate enhanced the so-called " alkaline reserve " of a crankcase oil, enabling it to counteract acidic contaminants. He also found that treatment of the basic sulphonate with carbon dioxide converted it to a sulphonate–metal carbonate complex which he characterized as having ". . . the same total alkaline reserve, although not as strongly basic in character as the hydroxide complex."

Other researchers such as Watkins [25] and McNab [26] suggest that basic sulphonates are classical basic salts which can be represented, in the case of barium, by the structure :



It should be noted, however, that they offered no experimental data to support their opinion. Furthermore, their suggested structure does not accommodate basically-reacting sulphonates which possess more than twice the theoretical amount of metal.

There has been no definitive, published research which would serve to clarify the structure chemistry of basic sulphonates. As to their efficacy as detergent additives there is little controversy, however. A large proportion of the sulphonate additive currently used in detergent oils in the U.S.A. is of the basic sulphonate type.

Reasons for the efforts made to " pack in " as much neutralization capacity as possible into a basically-

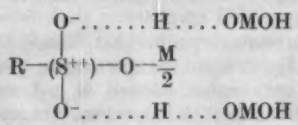
reacting detergent additive were previously advanced. By means of conventional techniques, *i.e.* simply heating sulphonates with a large amount of metal base, it has been determined that for petroleum sulphonates no more than about three times the theoretical amount of metal can be incorporated if the resulting basic sulphonate is to possess satisfactory oil solubility characteristics.

In recent years, however, ways have been discovered to prepare fully oil-soluble sulphonates which contain from three to as much as ten times the theoretical amount of metal. Such " overbased " sulphonates not only possess great neutralization capacity, but they also appear to possess unusually high dispersive power. Their high dispersive power may be a direct consequence of their high percentage of polar, inorganic base with its postulated affinity for polar contaminants found in oxidized oils.

These overbased sulphonates are formed when an oil-soluble sulphonate or sulphonic acid is heated with a large proportion of metal base in the presence of a relatively small amount of a " promoter " or catalytic agent.[27] The promoter is preferably a phenolic compound, although it may be an ionizable atom such as, for example, aci-nitro compounds, organic acids of phosphorus, aromatic carboxylic acids, enolic carbonyl compounds, and the like.

A striking illustration of the almost unbelievable amounts of inorganic base which can be incorporated in a sulphonate by a promoter-catalysed process is shown in example 12 of U.S.P. 2,695,910. In this example, barium petroleum sulphonate is reacted with barium oxide in the presence of di-*iso*butyl-phenol (the promoter) and carbon dioxide to produce a fully oil-soluble, overbased sulphonate containing about nine times as much metal as the normal sulphonate.

The structure of these overbased sulphonates is not known. They may be sulphonates which contain large amounts of colloidally-dispersed metal base, or, on the other hand, they may be complexes in which the metal base is incorporated by virtue of hydrogen bonding as in the postulated structure :



where M represents a divalent metal.

Van Ess[28] prepares an overbased sulphonate by dispersing a metal alcoholate in an oil-soluble sulphonate and subsequently treating the dispersion with sufficient water to hydrolyse the alcoholate to the corresponding metal hydroxide.

Using this technique, he was able to prepare an oil-soluble, overbased magnesium sulphonate containing about six times as much metal as found in the normal sulphonate. Although he was unwilling to commit himself, Van Ess suggested that the magnesium hydroxide might be held in the sulphonate by secondary valence forces, as in the postulated Werner-type co-ordination complex :

Still another process for preparing overbased sulphonates is described by Vinograd *et al*,[29] who first prepare a colloidal metal base in alcohol and then add it to an oil-soluble sulphonate. The resulting products are colloidal dispersions in which the colloidal particle size is stated to lie between 0·001 and 1·0 μ.

In recent years, basically-reacting detergent oils have been in ascendancy owing to their ability to neutralize harmful " petroleum oxyacids " and acids originating from blow-by fuel combustion products and provide a high level of detergency. Denison *et al*[30] have advanced a theory to account for the greater efficacy of basically-reacting detergent additives as compared with non-basic or neutral additives.

They showed experimentally that certain oxidation products of mineral oils, termed " petroleum oxyacids," undergo condensation reactions and precipitate from the oil on to hot metal surfaces to form deposits of gum and lacquer. It is proposed that basically-reacting detergent additives prevent these reactions from occurring by combining with the oxyacids to form inert, oil-dispersible or oil-soluble salts. They also suggest that basically-reacting detergents are capable of " washing " away freshly deposited oxyacids from hot engine parts, but are not effective once the oxyacid molecules have condensed or polymerized to tightly adherent, insoluble deposits.

Palmer[30] reports that the use of a heavy-duty lubricant * meeting U.S. Army Ordnance Specification MIL–O–2104 † in automobile passenger car service increased cleanliness on the average by 25 per cent and reduced piston ring and cylinder bore wear on the average by 37 per cent and 42 per cent, respectively. The reduction in wear over that obtained with an uncompounded mineral oil lubricant reflects the ability of the basically-reacting detergent additive to neutralize and render harmless the acidic contaminants which cause corrosive wear of the ferrous surfaces of an engine.

As reported by Zuidema,[31] the principal function of detergent oils is to disperse and to retard the flocculation or coagulation of contaminants such as soot, resins, and petroleum oxyacids which form during the operation of internal combustion engines and tend to deposit on the engine parts.

Detergency in aqueous or other ionic media has been shown to be colloidal phenomenon in which normally insoluble contaminative particles are adsorbed in soap

* Known by the authors to contain a basically-reacting detergent additive.

† Specification number was subsequently changed to MIL–L–2104A.

micelles, with the polar portion of the soap molecule extending towards the ionic medium and the non-polar portion being adjacent to the contaminant.

The mechanism of detergency in non-aqueous, non-ionic media such as mineral oils is not fully understood. However, based on the studies of Arkin *et al*,[32] who found evidence for existence of soap micelles in non-aqueous media, there is good reason to believe that detergent oils may act at least in part in a manner similar to aqueous soap solutions. From a theoretical standpoint, the character of the micelles in a detergent oil would be quite different from those present in the ionic system discussed in the previous paragraph. In a mineral oil system the polar portion of the detergent additive would be adsorbed on the contaminant and the non-polar portion would extend towards the oil.

Further evidence of an indirect nature to support the mechanism of detergency advanced above is found in the chemical composition of detergent additives themselves. All commercial detergent additives of proven effectiveness possess in common an oleophilic, non-polar group and an oleophobic, polar group.

Suspension and soiled cloth washing techniques employing either carbon black or graphite as the contaminant have long been used to evaluate the detergent power of soaps for aqueous systems.[33] It is hardly surprising, therefore, that early attempts to measure the effectiveness of detergent oils outside of an engine should rely on closely related techniques.[34] More highly specialized bench tests which are contingent on the ability of a detergent additive to retard the separation of asphaltenes from oil [34] or reduce the build-up of "coke" or lacquer-like deposits on hot metal panels [35] have also been proposed.

One of the most recently reported bench tests for detergency involves the microscopic examination of a used oil at various elevated temperatures extending from 60° C to above 200° C.[36] The resistance of the contaminative particles in the oil to flocculation with increasing temperature is taken as a measure of the detergent power of the oil.

As in the case of bench EP lubricant testers, detergency bench tests have sometimes provided a means for eliminating very inferior additives. However, none has yet proved equal to the task of predicting the relative effectiveness of different detergent oils in full-scale engines with a satisfactory degree of accuracy and reproducibility. Taken as a whole, they have been less useful as research tools for the development of detergent oils than have bench EP lubricant testers for the development of hypoid lubricants.

In all probability this situation exists because bench tests for detergency measure only one or at best very few characteristics of a detergent oil such as dispersive ability or heat stability in a relatively simple, predetermined environment. The environment presented to a lubricating oil by an operating internal combustion engine is infinitely more complicated. Here there are, for example, periods of activity and inactivity, temperatures ranging from ambient temperature to well above 200° C, catalytic oxidation zones formed by the metal surfaces of the engine parts, turbulent and relatively quiescent zones, zones of high mechanical shear, combustion products such as soot, acids,* and water, and foreign matter introduced by virtue of the intake air and crankcase ventilation systems. All of these factors and perhaps many others which have not been mentioned have their influence on the amounts and kinds of contaminants with which the detergent oil must cope. Thus, if one were to attempt to fashion a test device which would faithfully reproduce these factors, the chances are that the resulting device would be as complicated as an engine itself. So, it might be suggested, why not use an engine and avoid all of the errors inherent in the extrapolation of test results from one device to another?

As further evidence of the sensitivity of detergency evaluations to well-nigh intangible factors, consider the difficulty not infrequently encountered in obtaining good correlation between full-scale detergency tests conducted in the laboratory and out in the field.

Although accelerated high temperature tests of detergent oils in laboratory engines, particularly diesel engines, have correlated well with results obtained in high-temperature field service of diesel or gasoline powered equipment, a detergency evaluation in intermittent, relatively lower temperature engine operation, as typified by door-to-door delivery truck service, is often quite different from an evaluation based on laboratory engine tests. In the latter case, attempts have been made to improve the degree of correlation by specifying the operation of the laboratory engine at varying speeds and purposely sub-normal crankcase and water jacket temperatures.[37] While such test procedures have reflected to a limited extent the severe deposit and sludge conditions prevalent in intermittent, low temperature field service, they cannot replace field tests for a definitive evaluation of detergency in this type of service.

What has been said emphasizes that detergency is not an absolute or static property. An additive which shows marked detergent properties in continuous, high-temperature engine service is not necessarily effective in intermittent, low-temperature service, and vice versa.

Summarizing this discussion concerning detergent additives and their mode of action, it may be said that it is the task of a detergent oil to keep engine parts such as pistons, rings, oil screens, hydraulic valve lifters, crankcase pans, and the like clean and free from harmful deposits which would impair the efficiency of the engine. Although the ability of a detergent oil to disperse contaminants and maintain them in suspension is a very important factor in the

* In the case of fuel oils, the acids are predominantly sulphur acids such as sulphurous and sulphuric acids derived from the sulphur which is present in virtually all commercial diesel fuels. In the case of gasoline, hydrobromic and hydrochloric acids are formed from the halogen containing scavengers used to minimize deposits caused by TEL.

performance of this task, it is believed that other factors—many of which have not yet been characterized—also play an important role. Foremost among these other factors is the ability of the detergent oil to neutralize and render harmless the deposit-forming, wear-accelerating acidic bodies coming from oil oxidation and fuel combustion products.

A modern lubricating oil invariably contains anti-oxidant and anti-corrosion additives as well as one or more detergent additives.

The antioxidant retards the formation of harmful, deposit-forming oxidation products such as petroleum oxyacids and thus, in a sense, assists the detergent in performing its intended role. Since many detergents behave as pro-oxidants, the incorporation of an anti-oxidant in the detergent oil is generally required for satisfactory overall performance.

The anti-corrosion additive (which in some instances also serves as the anti-oxidant) protects sensitive bearing surfaces from the corrosive action of acidic bodies in the oil. The choice of an anti-corrosion additive is not always a simple matter. Most anti-corrosion additives function by reacting chemically with the metal surface of a bearing to deposit thereon a film which is more or less impervious to attack by acidic bodies in the oil.[38] Since detergents tend to loosen and disperse deposits, they presumably could act to remove the protective film on the bearing surface and thereby leave that surface bare and vulnerable to corrosion.[39] Thus, the anti-corrosion additive must form a tightly adherent film which the detergent will not remove if bearing corrosion is to be held within acceptable limits.

Detergent oils are currently available in the U.S.A. in several different grades representing different degrees of " levels " of additive treatment.

The amount of detergent additive used in a detergent oil varies according to the severity of anticipated service conditions.

At present, three grades of detergent oils are recognized by the petroleum industry in the U.S.A. In the order of increasing detergent power, they are: " MIL-L-2104A," " Supplement 1," and " Series 2 " oils.

The first listed grade—the most widely used of the three—designates an oil which will give satisfactory performance in a one-cylinder Caterpillar diesel engine operated for a total of 480 hr [40] on fuel containing a minimum of 0·35 per cent sulphur. The severity of this test is such that as far as known, no uncompounded oil or oil containing only inhibitor type additives will give an acceptable result.[41] In addition, the oil must also give satisfactory performance in a gasoline engine test [42] especially designed to evaluate the oxidation and corrosion inhibiting properties of a lubricant. The designation MIL-L-2104A stems from the U.S. Ordnance Engine Oil Specification of the same title which sets forth the above-noted performance requirements.

Next is the so-called " Supplement 1 " oil. Both laboratory and field test experience convinced the petroleum industry that a level of detergency higher than that provided by a MIL-L-2104A oil is desirable where diesel engines are operated on fuel containing 1 per cent or more of sulphur. Since a substantial proportion of the diesel fuel available in the U.S.A. contains sulphur within this range, it became important to provide a grade of detergent oil which would assure satisfactory engine cleanliness when such fuels were used. To qualify an oil for this type of service, the petroleum industry specifies the same tests found in the MIL-L-2104A specification, except that fuel containing a minimum of 1 per cent sulphur is to be used in the Caterpillar diesel engine test.

A still higher level of detergency than that supplied by a Supplement 1 oil is desirable where supercharged diesel engines are operated on high sulphur content fuel. In typical supercharged diesel engine operation, speeds, oil temperature, coolant temperature, fuel consumption, and power output are all substantially higher than in conventional engine operation. The detergency requirements inherent in such service are so high that oils of the MIL-L-2104A and Supplement 1 levels generally fail to maintain a satisfactory state of engine cleanliness. A category of detergent oils known as Series 2 oils was created to provide lubricants which would give acceptable performance under these very severe service conditions. To qualify under the Series 2 specification promulgated by the Caterpillar Tractor Co., an oil must give satisfactory performance in a supercharged, one-cylinder diesel engine test of 480 hr duration using fuel containing a minimum of 1 per cent sulphur.[43]

Very recently, the Caterpillar Tractor Co. found it necessary to raise the already exacting performance standards for Series 2 oils. Laboratory and field experience with a new, small bore, six-cylinder, highly supercharged diesel engine of advanced design indicated that existing Series 2 oils failed in many instances to maintain a satisfactory degree of engine cleanliness. Working closely with the petroleum and additive industries, the Caterpillar Tractor Co. established very high but attainable performance standards which called for a test of 480 hr duration in the new engine using high sulphur content fuel.

To realize a satisfactory state of engine cleanliness in this test, it was found that the amount of detergent additive had to be increased as much as two-fold over previous Series 2 levels. Some idea of the severity of the new test can be gained from a knowledge that lubricants giving acceptable performance contain a total of from 15 to 25 per cent additive, substantially all as detergent additive.

These improved Series 2 lubricants have been in the field for several months now, and reports indicate that their performance is measuring up to expectations.

It is evident that little exact knowledge is available on the mode of action of detergent additives or the structure chemistry of basically-reacting detergent additives. There has been, however, much progress in the empirical art of producing effective detergent additives and lubricants which will some day be

paralleled by similar progress in the field of fundamental studies.

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DISCUSSION

R. Tourret: At the Admiralty Oil Laboratory, we are very interested in the performance of detergent oils of the MIL-L-2104A and Supplement I quality levels in diesel engines in use in the Royal Navy. Would the authors care to comment on the effect of salt-water contamination on the engine performance of such oils?

C. V. Smalheer: MIL and Supplement I level lubricants have been found satisfactory by the U.S. Navy for use under conditions of service where salt-water contamination is present.

U.S. Navy specification MIL-L-17778A of 25 March 1955 calls for GM-71 diesel engine tests of Supplement I lubricants containing salt water as a contaminant. The specification states: "The oil, even when contaminated with sea water, shall be suitable for all types of diesel engine bearing materials, shall not cause either excessive ring sticking or clogging of oil channels, shall keep cylinder and ring wear down to a minimum, and shall not cause excessive lacquer, carbon, or sludge deposits on any part of the engines in which it is intended for use."

U.S. Navy specification 9000B is quite similar and requires satisfactory performance of MIL level oils in the presence of sea water as a contaminant.

Many Supplement I and MIL-L-2104A lubricants have been qualified under these exacting specifications.

J. S. Elliott: I would like to ask the authors if they could enlarge on the reason for the apparent incompatibility of certain additives with respect to the high speed and high torque tests referred to on p. 340.

Why, for example, should the presence of a carboxylic ester, as indicated in Table I, interfere with the action of the E.P. additives, presumably sulphur and chlorine compounds normally present?

C. V. Smalheer: There is no definitive, fundamental knowledge which can be used to explain the performance incompatibility between certain types of E.P. additive such as carboxylic esters and active sulphur compounds. That this incompatibility exists has been proved repeatedly in our laboratories.

If one were to speculate, it could be imagined that each incompatible E.P. additive when used alone reacts with a gear surface under boundary conditions to form a very specific type of film which is the actual, effective lubricant. If two such incompatible additives, *e.g.* carboxylic ester and active sulphur compound, are present together in a lubricant, the active sulphur compound may form its "high speed" protective film rapidly and completely on the contacting surfaces under E.P. conditions, thereby preventing the carboxylic ester from reaching the metallic gear surface to form its "high torque" protective film. Furthermore, the carboxylic ester may alter the character of the film formed by the active sulphur compound so that the resulting modified film is less effective than it would be ordinarily.

The net result of this hypothetical set of occurrences would be poor performance of the lubricant in both high speed and high torque service.

B. E. Hurley: Passing reference is made to "ashless" additives and V.I. improvers. Would the speaker comment on "ashless" additives, especially those pro-

duced by treating an oil with an electrical brush discharge?

With reference to V.I. improvers—what are they, how do they work, and how do they behave under high rates of shear?

Apart from the destructive shearing of the polymer, what other information can the speaker give regarding apparent viscosity and behaviour in the film breakdown region?

C. V. Smalheer: There is very little published information outside of patents on the subject of ashless detergent additives. From work done in our laboratories, it can be predicted with a fair degree of assurance that an effective ashless detergent will contain both oleophilic and oleophobic groups within the molecule.

Much research has been carried out, principally in Europe, on brush discharge treated ("voltolized") oils and their utility in the lubrication field. The literature in this field of endeavour is both voluminous and contradictory. However, an excellent critical summary by C. L. Thomas, G. Egloff, and J. C. Morell * has been published. Voltolized oils have not been studied in our laboratories. Consequently we are not prepared to discuss their merit as oil additives.

V.I. improvers are oil-soluble organic compounds, principally high polymers, which diminish the rate of change in the viscosity of an oil with increasing temperature. All effective V.I. improvers "thicken" an oil perceptibly. This thickening effect, with its relative constancy over a wide temperature range, operates to lessen viscosity change with temperature variation.

V.I. improvers differ widely in their behaviour under high rates of shear. Some lose substantially all their initial thickening and V.I. improving power on being subjected to drastic shear for as little as one hour at elevated temperatures. Others, however, are quite stable under the same conditions. There is evidence which indicates that the greater the degree of cross-linking in a polymeric V.I. improver, the lower is its resistance to shear.

No studies have been made in our laboratories on the subject of apparent viscosity and behaviour of V.I. improvers in the film breakdown region.

B. E. Hurley: Does it not strain one's credulity that a molecule with oleophilic and hydrophilic poles shall do other than stabilize oil–water emulsions?

C. V. Smalheer: It does strain one's credulity somewhat to observe that a molecule with oleophilic and hydrophilic poles can do other than stabilize oil–water emulsions. Yet this does occur. There is more to this observed effect than the simple presence of oleophilic and hydrophilic poles in the same molecule. For example, there is the very important factor of the relative solubility of the detergent additive in oil and water, respectively. A sodium mahogany sulphonate detergent is very soluble in both water and oil. When it is added to an oil–water emulsion it does indeed stabilize such an emulsion. On the other hand, a barium mahogany sulphonate detergent, which is very soluble in oil but only slightly soluble in water, has comparatively little stabilizing action on oil–water emulsions.

Thus, by taking into consideration the solubility behaviour of the detergent in oil and water and making the choice of the detergent additive accordingly, emulsion problems involving either fresh or salt water can be avoided in commercial practice.

R. Leslie: Would you not consider that water plays a considerable part in (1) the structure of basic metallic sulphonate oil systems, and (2) the adsorption of metallic sulphonates on metal surfaces?

It is felt that, as regards (1), the solubilization theory to explain the incorporation of high alkalinity is discounted because of the equally high amounts of water which would be required to be simultaneously present to dissolve the base. The amounts of water in such basic sulphonates are very small, and the complex-formation theory is therefore favoured.

As regards (2) in the absorption of, for example, barium sulphonate on a metal surface, is it the case that barium atoms are "freed" at the surface and must require traces of moisture to stabilize them, in which case some alkalinity is produced from even a neutral sulphonate?

C. V. Smalheer: Water may or may not play a part in the preparation and structure of basic metallic sulphonate systems. A review of the published literature, principally patents, reveals that water generally does perform an important if not essential role in most processes for the preparation of basic sulphonates. There are many successful procedures, however, for the preparation of highly "overbased" sulphonates under substantially anhydrous conditions.

It is our belief that the "solubilization" theory to explain the formation of basic sulphonates cannot be discounted even when only minor amounts of water are present during manufacture. Perhaps the word "solubilization" is not well chosen, since solubilization in the detergent phase and not the aqueous phase is intended. It would be better to say "peptization," which Webster defines as "to bring into colloidal solution; to convert into a sol." It is entirely possible that water, even in small amounts, can act as a transient medium for the rupture of large size particles of metal base into particles of colloidal size. Once the metal base has been reduced to colloidal particles, it can then enter the detergent phase. In this connexion, electron microscope studies indicate that colloidal particles are present in basic detergents.†

No studies have been made in our laboratories on the subject of water and its effect on the adsorption of metallic sulphonates on metal surfaces. It is highly probable that water materially affects the extent of adsorption. Another equally important factor, however, would be the relative solubility of the particular metallic sulphonate in oil and water, respectively. In our answer to one of Mr Hurley's questions it was noted that different metallic salts of a given sulphonic acid can differ widely in their solubility behaviour.

We have no evidence that a neutral barium sulphonate generates "free" barium atoms on a metal surface during adsorption or that these barium atoms are converted to barium hydroxide by traces of moisture. In view of the relative position of barium and iron in the electromotive series, the freeing of barium atoms on the metal surfaces appears unlikely. We incline toward the physical adsorption theory, where the $-SO_3$ metal portion of the sulphonate would be oriented on the metal surface.

---

* Thomas, C. L., Egloff, G., and Morell, J. C. *Chem. Rev.*, 1941, **28**, 1–70.

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OBITUARY

OLIVER THORNYCROFT, C.B., O.B.E., M.A., M.I.Mech.E., F.R.Ae.S., F.Inst.Pet.

1885–1956

OLIVER THORNYCROFT was born in April 1885, the only son of Sir Hamo Thornycroft, the famous sculptor, and a nephew of Sir John I. Thornycroft, F.R.S., of marine engineering fame.

After a general education at Bedales School he went up to Cambridge in 1903. Though my father and Sir Hamo were friends, I had in fact never met Oliver until we both arrived at Cambridge University, he in Clare College and I in Trinity. Almost immediately we struck up a close friendship which endured until his sad death on 24 August last.

At Cambridge we both attended the same lectures and we both spent a great deal of time in the University workshops. My chief interest at that time was in heat engines of all sorts, and O. T.'s in electrical machinery, but we were both equally interested in the automobile, which, at that date, was just emerging from the stage of being a fascinating but wayward toy to that of a practical vehicle.

At Cambridge O. T.'s charm and delightful frankness brought him a wide circle of devoted friends, most of whom, unhappily, were killed in the holocaust of the first world war. Apart from technical matters, O. T.'s chief hobby was mountaineering, and this, at Cambridge, had to take the form of roof climbing! Sometimes he would stay with me in my rooms at Trinity until after midnight, when our College gates were closed, and then climb out of my window and thence by way of the rooftops to his own College, Clare, often decorating somebody's chimney-pot on the way.

From Cambridge O. T. served an apprenticeship with the firm of Westinghouse (later Metro-Vick) at Trafford Park, Manchester, while I joined my grandfather's firm of Rendel, Palmer & Tritton, Consulting Civil Engineers. After his apprenticeship O. T. joined me at Rendel's as our expert on electrical problems. At that time the firm was engaged on a number of large bridge-building undertakings, for the erection of which a good deal of specialized equipment was required, mostly electric, hydraulic, and pneumatic. O. T. dealt with the electrical problems while I struggled with the mechanical ones, but we shared common ground in our love for the internal combustion engine, though at that time it played little or no part in Civil Engineering.

At the outbreak of the first world war, O. T. volunteered for active service, but, after many vicissitudes, found himself, together with several of our Cambridge friends, a member of a somewhat piratical group known officially as Squadron 20, Royal Naval Air Service, a singularly inappropriate title, since the squadron had nothing whatever to do with either the sea or the air. Of this group the chief moving spirit was Sir Albert Stern.

This more or less lawless and independent group set itself to work to develop what later came to be known as the tank. In this task it enjoyed the benevolent smiles of both Winston Churchill and Lloyd George, and the active help of Sir Eustace Tennyson D'Eynecourt, then Director of Naval Construction at the Admiralty. Though for the most part very youthful, it comprised a very large measure of engineering talent and of imaginative genius and, above all, of superb co-operation, under Stern's leadership and drive. In this development O. T. took a leading part, first on the design side, and then in charge of all the experimental work and testing, which he carried out with outstanding ability. At that time not only was no suitable engine available, but all the recognized designers and manufacturers of high-speed engines were already fully occupied with work of high priority. At O. T.'s suggestion I was invited to design an engine for the purpose, and, with the help of my grandfather's firm, to organize the production of such engines by a group of firms accustomed normally to building large slow-speed gas and diesel engines. Thanks to the most generous help on all sides and to a very large slice of good luck, the project turned out a success. I had felt very diffident about undertaking it, for my experience was indeed very limited, but O. T. was very pressing and encouraging and gave me much advice and practical help, which indeed proved invaluable.

Until the end of the first world war O. T. remained in charge of all the testing and development work on the tanks, the success of which was due so largely to his extreme thoroughness, his wide theoretical and practical knowledge, and to the respect and loyalty which he always commanded. For his achievements in this enterprise he was awarded the O.B.E.

During the war I had become so involved with, and so fascinated by, the internal combustion engine that it became my ambition, with the help of friends, to establish a laboratory for research into internal combustion engine problems and their fuels. In this project O. T. joined me and took the leading part, both in the management and organization of our laboratory and in the actual testing of engines and fuels. With his customary thoroughness he very soon became an accepted authority on fuels as well as on the engines which consumed them.

This happy collaboration of over twenty years lasted until 1940, when the Admiralty called for his services, first to help solve the urgent problem of how to deal with magnetic mines, and once that had been mastered to tackle the wider problems of anti-submarine devices. In all this work he played a very important part; the multiple mortar for throwing a pattern of depth charges, which proved so effective in combating the submarine menace, was one of his achievements, but his work during the last war was so shrouded in secrecy that even his closest friends knew little of what he was doing. That it was appreciated by the powers that be is shown by the fact that he was made Director of Aeronautical and Engineering Research at the Admiralty and awarded the C.B. At the age of sixty-five he officially retired from the Admiralty, but in fact remained at hand and fulfilled the very valuable role of Elder Statesman. At the same time he undertook a certain amount of private consulting work, where his wide experience and shrewd technical judgment must have proved invaluable.

Those who knew Oliver Thornycroft could not fail to be captivated by the charm of his personality, his modesty, his kindliness, and his obvious integrity. Those who worked with him admired the tenacity and thoroughness with which he tackled any project and the robust common sense that he always brought to bear on it. His death is a sad loss to the country as a whole, and a personal grief to all his friends.

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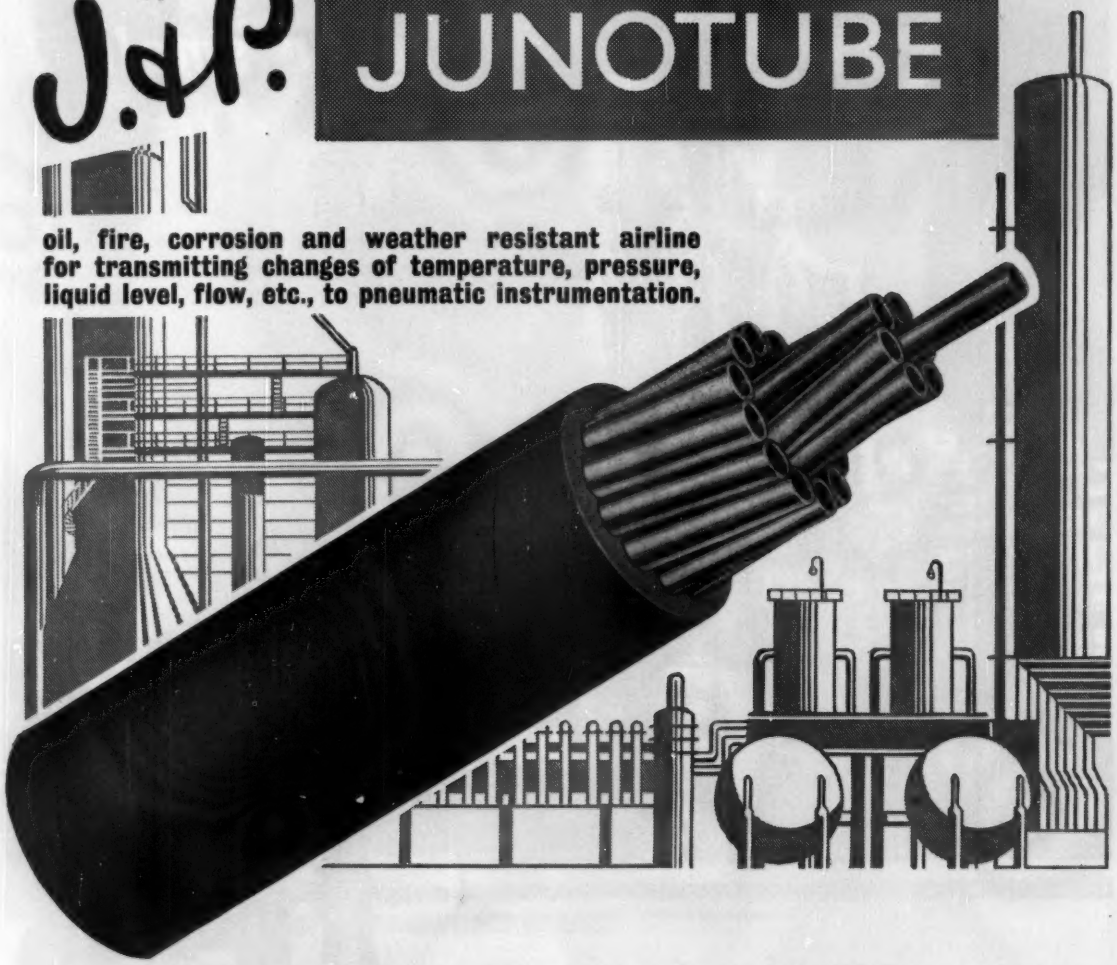

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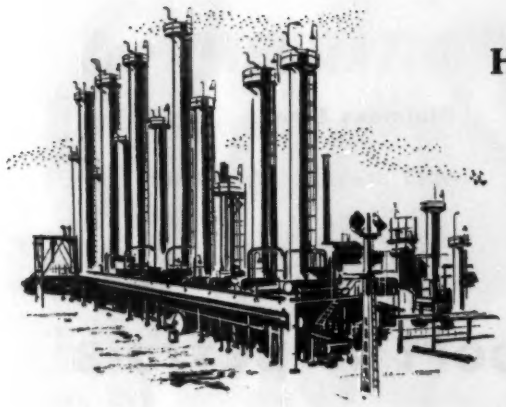

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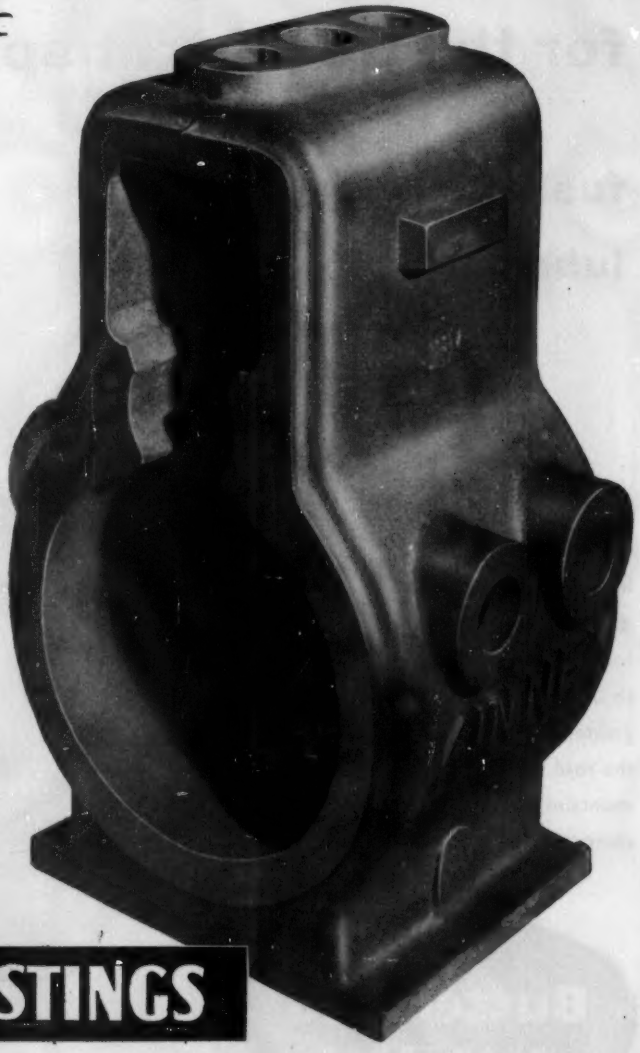

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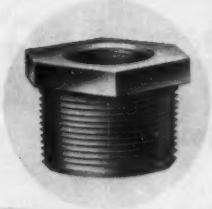

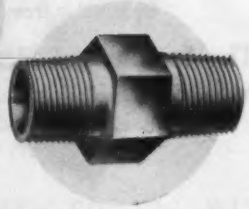

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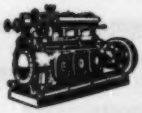

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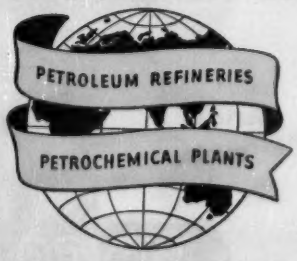

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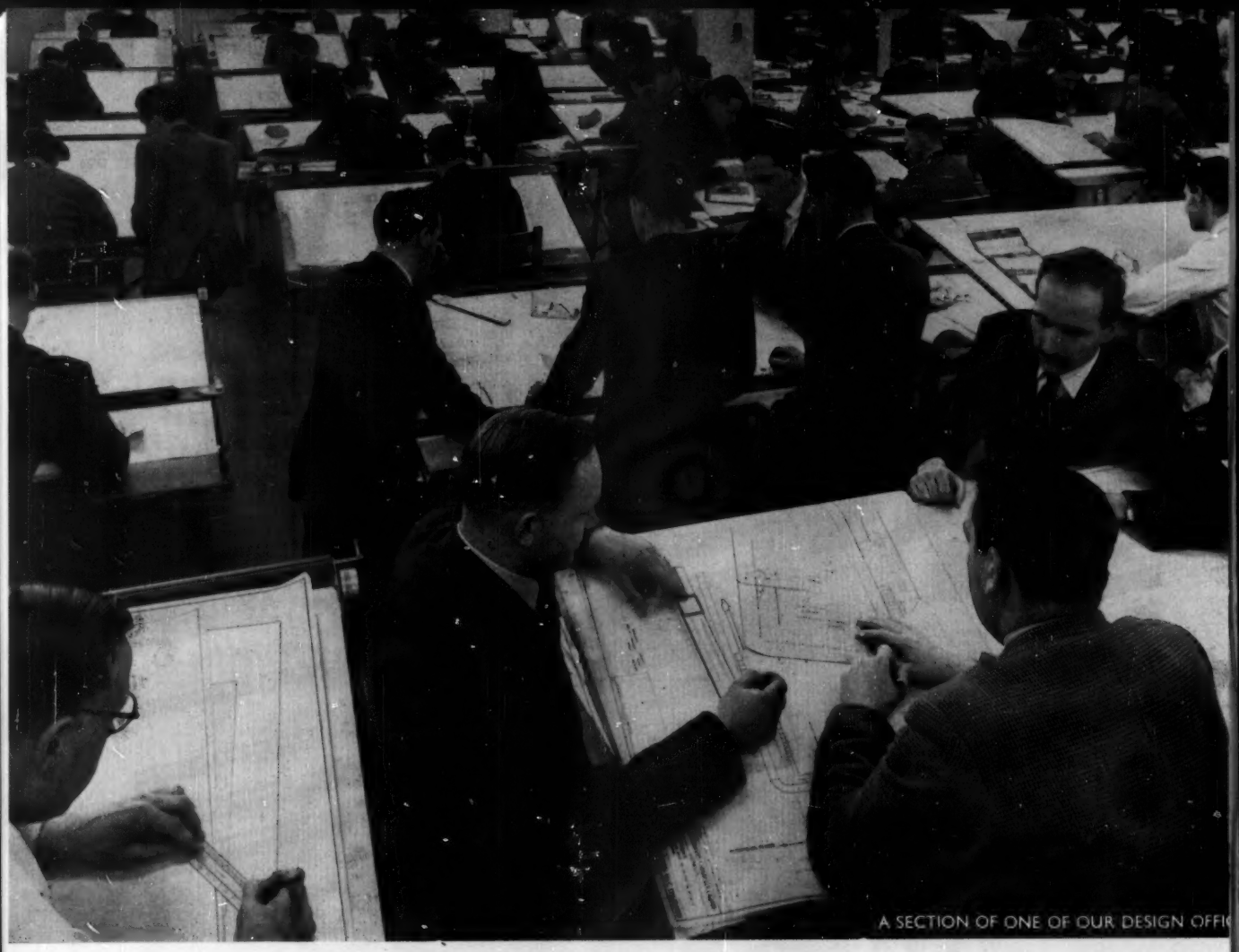

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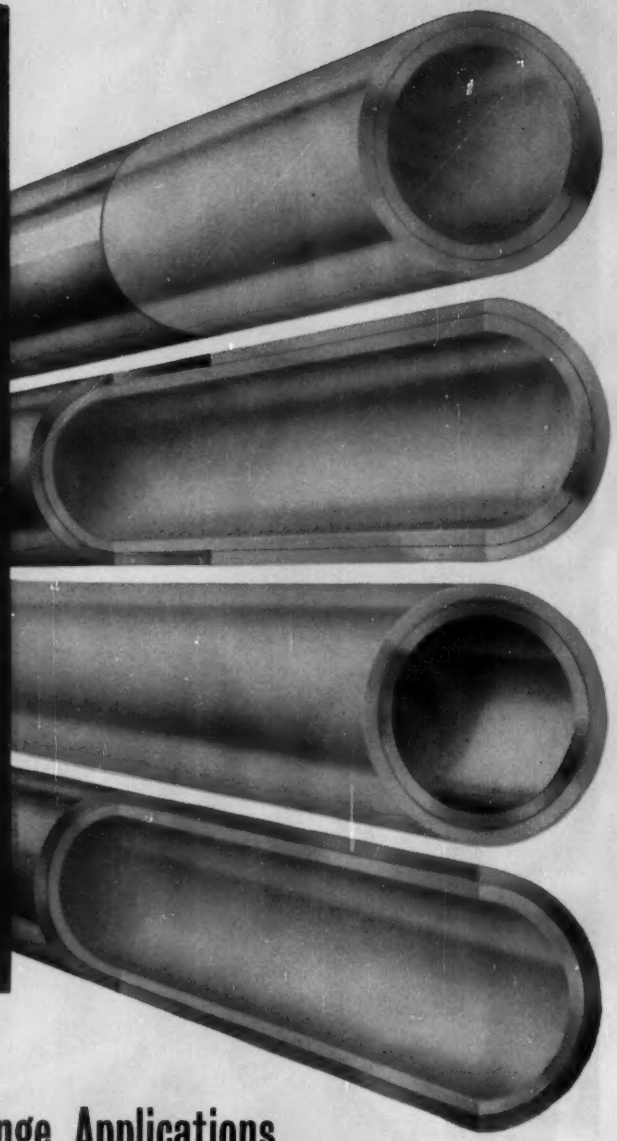

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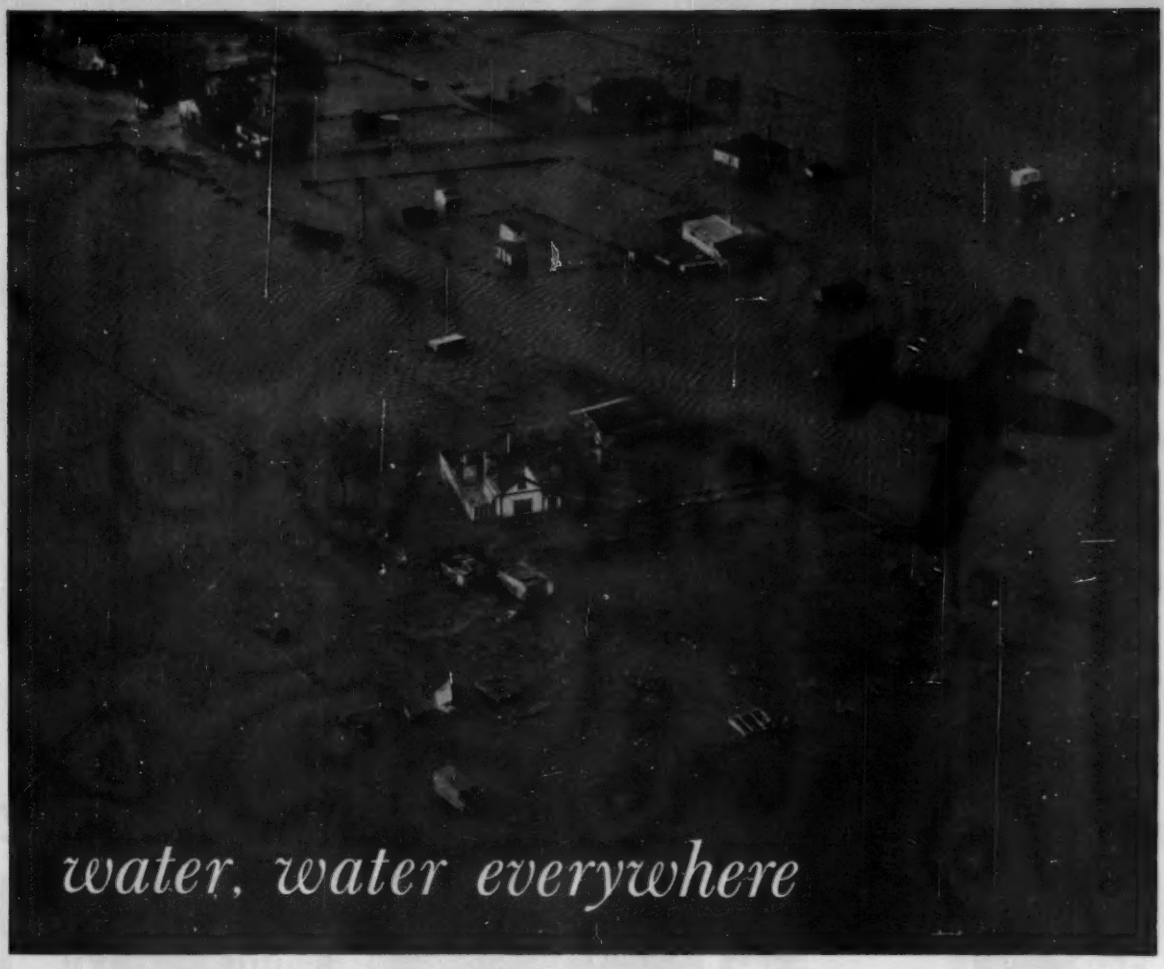

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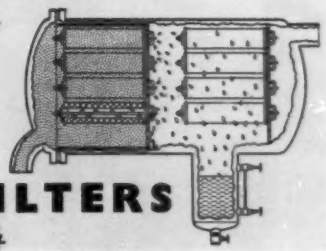

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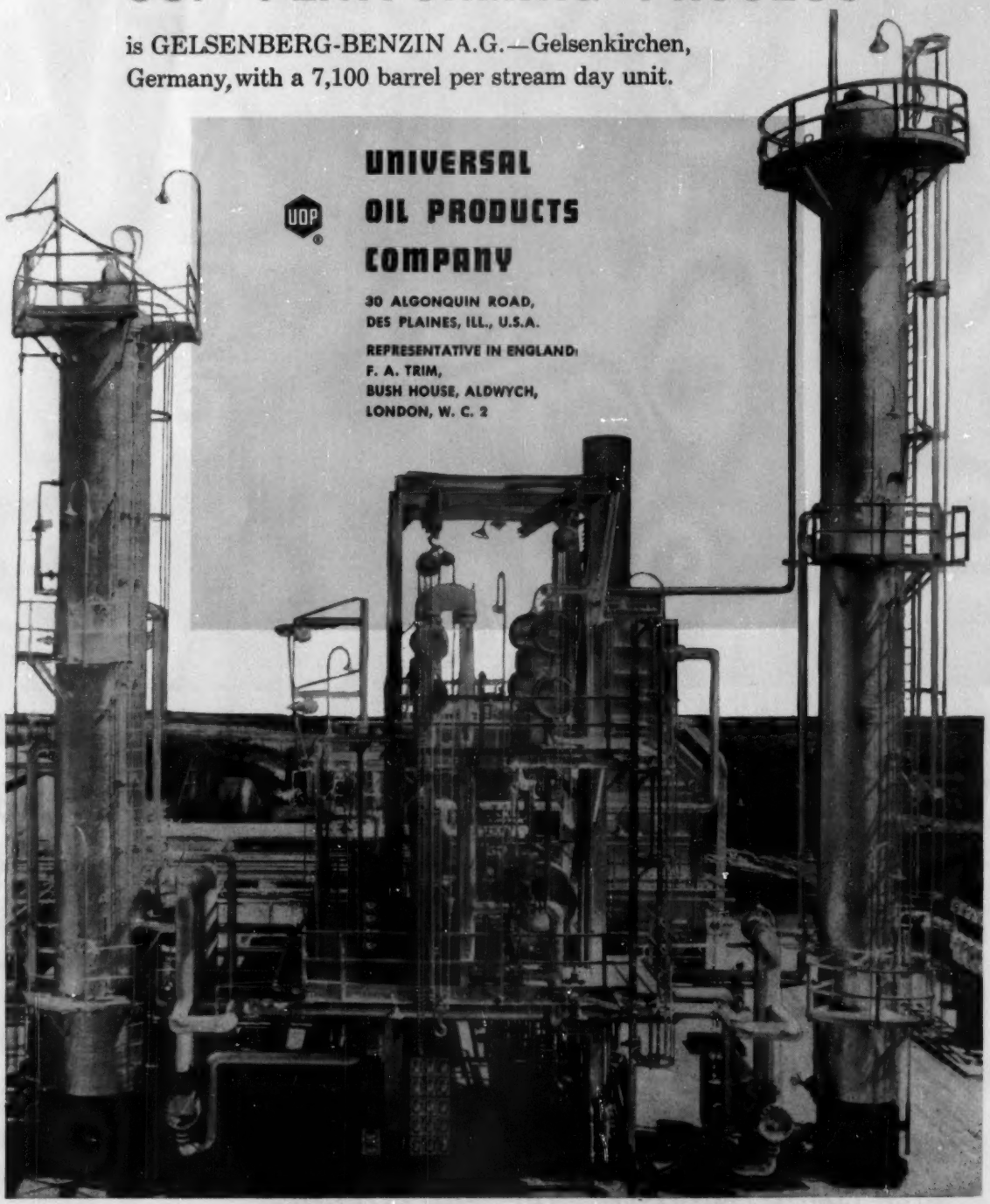

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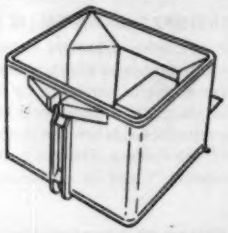
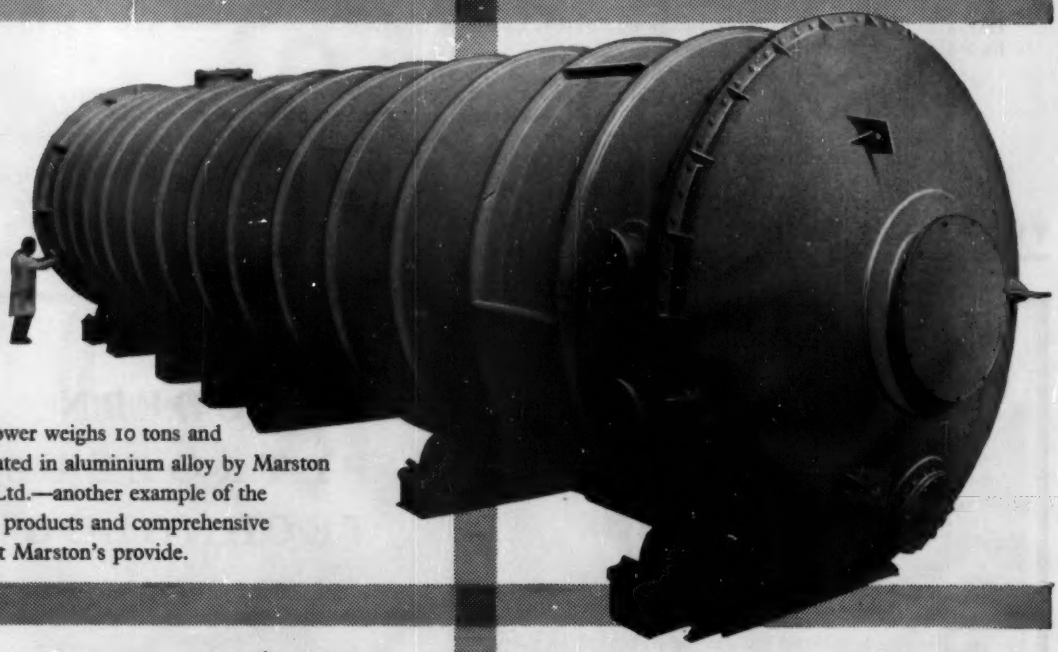
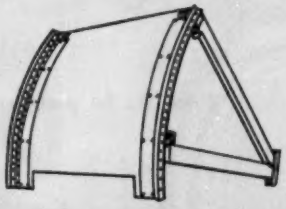


This truck-container is designed to carry granular material of particle size approximately $\frac{1}{10}$". Special attention had to be paid to the fit of the door and the smooth finish of the interior. The body ($\frac{3}{8}$" Plate Kynal M 39/2) was welded by the Argon arc and Argonaut processes.



This 52′ tower weighs 10 tons and was fabricated in aluminium alloy by Marston Excelsior Ltd.—another example of the specialised products and comprehensive service that Marston's provide.



This radial sluice-gate is 6′ 6″ wide and 6′ high. It is made of aluminium alloy, to minimise maintenance costs. To obtain a clean design free from any crevices where corrosion might start, the gate was welded by the Argon arc process. It is believed to be one of the first examples in this country of a radial sluice-gate in welded aluminium alloy.

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